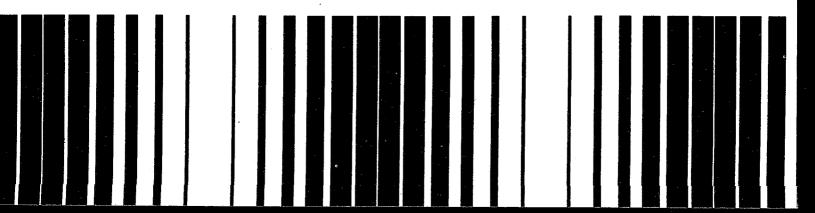
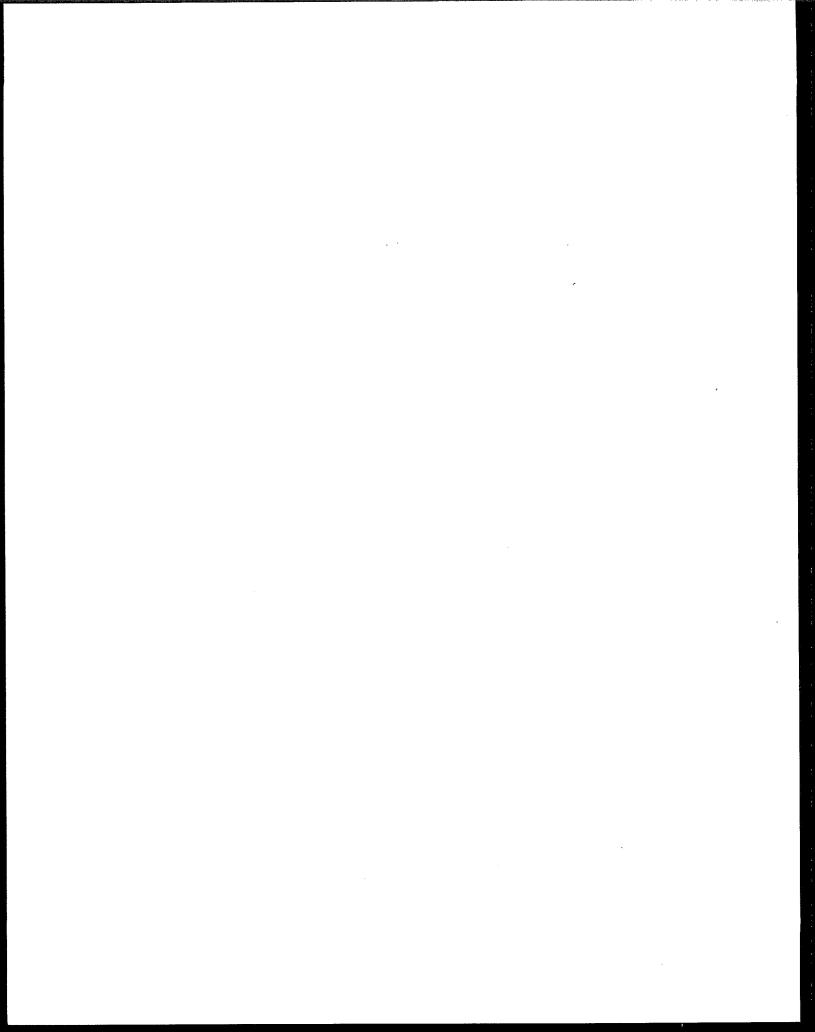


Seminars

Bioremediation of Hazardous Waste Sites: Practical Approaches to Implementation

May 20-21, 1993—Atlanta, GA
June 7-8, 1993—New York, NY
June 10-11, 1993—Chicago, IL
June 21-22, 1993—San Francisco, CA
June 24-25, 1993—Denver, CO





SEMINARS ON BIOREMEDIATION OF HAZARDOUS WASTE SITES: PRACTICAL APPROACHES TO IMPLEMENTATION

Office of Research and Development U.S. Environmental Protection Agency Washington, DC

April 1993

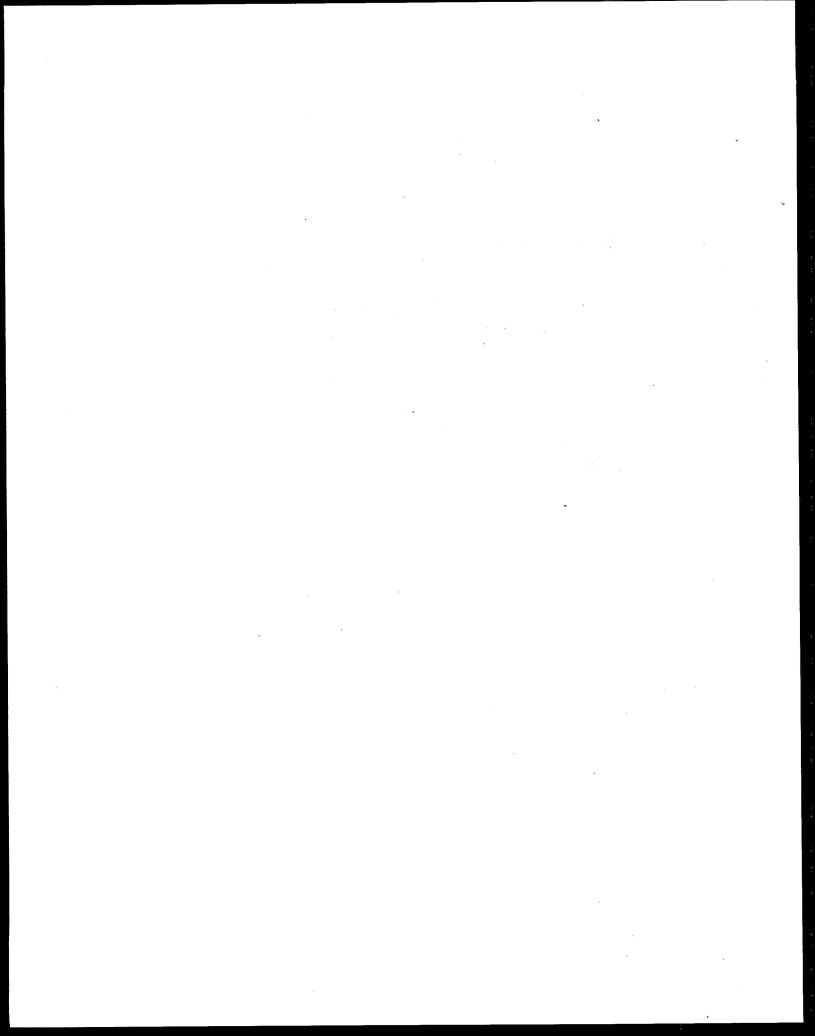


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Table of Contents

Progress in the Field Applications of Bioremediation	1-1
Background on Bioremediation	
Site Characterization Requirements	
reatability Studies	4-1
reatability Studies	5-1
Reactors for Treatment of Solid, Liquid, and Gaseous Phases	
oil Treatment: Land Treatment and Development and Evaluation of Composting	
echniques for Treatment of Soils Contaminated with Hazardous Waste	7-1
Bioventing	8-1
ubsurface Bioremediation	9-1



PROGRESS IN THE FIELD APPLICATIONS OF BIOREMEDIATION

John E. Rogers
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH

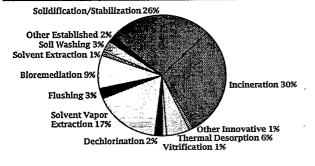
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Regional Representatives U.S. Environmental Protection Agency

Progress in the Field Applications of Bioremediation

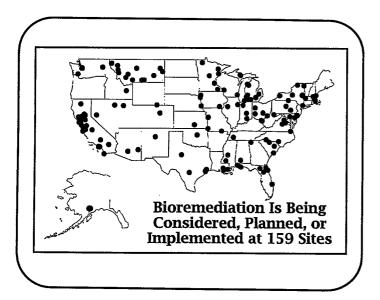
John E. Rogers
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH

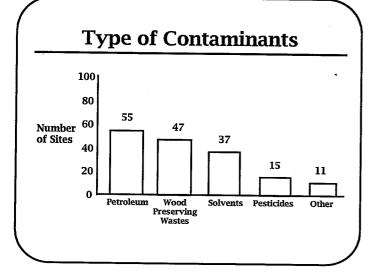
Selection of Treatment Technologies for Remedial Actions through 1991

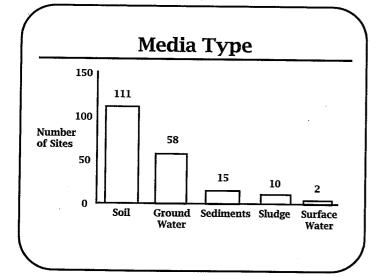


Bioremediation Database

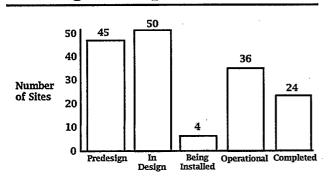
- Developing comprehensive national listing of CERCLA, RCRA, UST, TSCA, and pesticide sites using bioremediation
- Database includes information on contaminants, media, treatment selected, treatment efficiency, and costs
- Information available in quarterly bulletin currently and in computerized database in late 1993



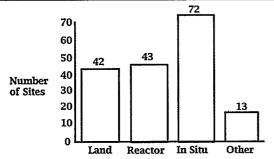




Stage of Implementation



Type of Treatment



Note: 149 sites have selected or implemented one or more bloremediation technologies

Treatment Type

- Ex situ land treatment
- Reactor treatments:
 - Activated sludge
 - **■** Fluidized bed
 - **Slurry**
 - Sequencing batch
 - Fixed film
 - Attached growth

Treatment Type (Continued)

- In situ technologies:
 - **■** Bioventing
 - In situ land treatment
 - Air sparging
 - Addition of nutrients, oxygen, hydrogen peroxide
- Other bioremediation :
 - Aerated lagoon
 - **■** Confined treatment facility
 - **Pil**e

Potential for Application of Bioremediation

- Solvents
 - **■** Contamination at 1,000 Superfund sites
 - Contamination at 1,000s of RCRA facilities
- Wood Preserving
 - 150 Superfund sites
 - 1,200 operating facilities

Potential for Application of Bioremediation (Continued)

- Petroleum
 - An estimated 2.1 million leaking UST
 - 15,000 oil spills annually
- Pesticides
 - 150 Superfund sites
 - 15,000 dealerships
 - Nonpoint sources

A. C.

BACKGROUND ON BIOREMEDIATION

Paul Flathman OHM Remediation Services Corporation Findlay, OH

INTRODUCTION

State-of-the-art bioremediation technology is being advanced on many fronts with exciting research programs and field applications being conducted throughout the world. Active areas of research and/or application include the development of novel methods for (1) treatment of chlorinated organics, such as polychlorinated biphenyls (PCBs), chlorinated aliphatics, and pesticides; (2) enhancing in situ biological treatment; (3) treatment of munitions, wood preserving, refinery, and manufactured gas plant wastes; and (4) treatment of volatile organic compounds (VOCs) using biofilters.

The objectives of this section are to:

- Introduce the concepts and terminology of bioremediation/biodegradation
- Discuss factors that influence biodegradation
- Explore benefits/limitations of bioremediation
- Provide an increased comfort level with this technology

The use of bioremediation is thought to be limited by an understanding of biodegradation processes, appropriate applications, control and enhancement in environmental matrices, and remediation costs. Bioremediation is an onsite, natural process. The residues from this process are typically nontoxic. The environment is minimally disturbed, and the process is cost effective compared to excavation followed by incineration and/or landfilling.

DEFINITION

Bioremediation is the manipulation of living systems to bring about desired chemical and/or physical changes in a confined and regulated environment. These desired changes include (1) the decomposition of toxic, hazardous compounds; (2) the improvement in environmental quality; and

(3) the reduction of human health risks. The process is not new. Land treatment (or solid-phase treatment) of contaminants in soil has been used for many years by the petroleum industry for the treatment of their wastes both in this country and throughout the world. Although while many of the organic compounds released to the environment are readily biodegradable, others are recalcitrant and persist. Many of these compounds are potentially toxic and their removal has received a high priority. Physical, chemical, or thermal treatment of these wastes is often very expensive. Biological approaches often provide effective, low-cost alternatives that also reduce the potential risk to human health and the environment.

BIOGEOCHEMICAL CYCLING

The biological oxidation and reduction of organic and inorganic compounds by living systems in the environment is a natural process. These changes primarily are brought about by the naturally occurring or indigenous bacterial and fungal populations within those environments. Ecology is the science that explores those interrelationships between organisms and their living (i.e., biotic) and nonliving (i.e., abiotic) environments (e.g., soil, ground water, and surface impoundment environments). The term ecological niche not only describes the physical habitat of a population of microorganisms in such an environment but also the functional role and the interactions of those microorganisms within that environment or ecological system (i.e., ecosystem).

Elements, such as the carbon found in phenol, an EPA priority pollutant, tend to circulate in characteristic paths or cycles between the biotic and abiotic portions of the environment. The term "biogeochemical cycling" describes the conversion and movement of materials by biochemical forces through the environment. Directly or indirectly, all biogeochemical cycles are driven by the radiant energy of the sun. Energy is absorbed, converted, and eventually dissipated within ecosystems (i.e., energy flows through ecosystems). The biogeochemical cycles involve physical (e.g., dissolution, precipitation, volatilization, fixation) and chemical (e.g., synthesis, degradation, oxidation-reduction) transformations of materials as well as various combinations of physical-chemical changes. The physical and chemical transformations also lead to the spatial translocations of materials, e.g., from the water column to the sediment and from soil to the atmosphere. All living organisms participate in the biogeochemical cycling of materials. Microorganisms, because of their ubiquity, diverse metabolic capabilities, and high enzymatic activity, play a major role in biogeochemical cycling.

Most elements are subject to some degree of biogeochemical cycling, but their cycling rates vary greatly. As might be expected, the major elemental components of living organisms (i.e., carbon, oxygen, hydrogen, nitrogen, sulfur, and phosphorus) are cycled most intensively. Minor elements (i.e., magnesium, potassium, sodium, and halogens) and trace elements (i.e., aluminum, boron, cobalt, chromium, copper, molybdenum, nickel, selenium, vanadium, and zinc) are cycled less intensively. The minor and trace elements iron, manganese, calcium, and silicon are exceptions to this rule. Iron and magnesium are cycled extensively in an oxidoreductive manner. Calcium and silicon, while minor components of protoplasm, form important exo- and endoskeletal structures in both micro- and microorganisms and consequently are cycled on an impressive scale. Nonessential and toxic elements, such as mercury, lead, and arsenic, also are cycled to some extent as evidenced by the methylation of mercury.

AEROBIC AND ANAEROBIC BIOREMEDIATION

With respect to the bioremediation of environments contaminated with hazardous organic contaminants, it is the energy-yielding portion of the carbon cycle that typically is enhanced. In this portion of the cycle, microorganisms, i.e., bacteria and fungi, play the key role of decomposers and convert carbonaceous organic matter into a form (i.e., carbon dioxide) the photosynthesizers or primary producers can use for the biosynthesis of "new" organic compounds. This decomposition of organic matter is an energy-yielding process which takes place in both aerobic (i.e., molecular oxygen-containing) and anaerobic (i.e., molecular oxygen-absent) environments. Some transformations of carbon occur under aerobic conditions while others occur only under anaerobic conditions. The generation of methane (or marsh gas) occurs only in anaerobic environments while the mineralization of alkanes, such as those found in petroleum hydrocarbons, is restricted largely to aerobic environments. This leads to a biogeochemical separation of living environments. Some organic compounds, such as the highly chlorinated PCBs, can accumulate in an aerobic environment and be unavailable to the biological community, while in an anaerobic environment, they can be transformed through a process referred to as reductive dehalogenation to less highly chlorinated PCBs, which might be amenable to aerobic biological treatment.

Energy in the form of heat and chemical bond energy is obtained by microorganisms through the energy-yielding metabolic processes of fermentation and respiration. Respiratory metabolism yields more energy to microorganisms than fermentative metabolism. In aerobic environments, respiration tends to be more prevalent than fermentation. Complete respiration results in the production of carbon dioxide, whereas fermentation normally results in the accumulation of low molecular weight organic alcohols and acids. If these fermentation products are transferred to aerobic environments, they are transformed to carbon dioxide by respiration.

The survival of a microorganism in a particular environment depends on how well that microorganism can meet its energy and organic and/or inorganic chemical requirements. Energy production by microorganisms is almost synonymous with the generation of adenosine triphosphate (ATP). ATP often is called the universal energy currency of the cell. Microorganisms are classified as autotrophs or heterotrophs based on whether they require preformed organic matter. Autotrophic microorganisms derive energy from either light absorption or oxidation of inorganic compounds. The chemoautotrophs of the nitrogen (i.e., nitrifers) and sulfur (i.e., sulfide- and sulfur-oxidizing bacteria) cycles are common examples of microflora that obtain their energy for the generation of ATP by the oxidation of inorganic compounds.

In heterotrophic metabolism, organic compounds, such as those on the list of EPA priority pollutants, are required for generating ATP. The parent compound (i.e., substrate) is transformed through a series of intermediary metabolites. Some metabolic pathways are common to most heterotrophic microorganisms. Such a pathway is the Embden-Meyerhof pathway of glycolysis which involves the conversion of glucose to pyruvate with a net gain of two moles of ATP and two moles of reduced nicotinamide adenine dinucleotide (NADH) per mole of glucose. The Embden-Meyerhof pathway is not the only glycolytic pathway, and pyruvate formed in these pathways is further metabolized. Under anaerobic conditions, these transformations often use the NADH (reducing power) generated during glycolysis to form a variety of organic end products and regenerate NAD. When there is no net oxidation in the overall pathway, the process is called fermentation. Different microorganisms carry out different fermentations. The end products of one organism's metabolism can be used to generate ATP by another organism, or even the same organism under different environmental conditions. Fermentation end products, such as ethanol, can be completely oxidized (i.e., mineralized) under aerobic conditions to yield additional ATP.

Under aerobic conditions, pyruvate can be oxidized to carbon dioxide with the generation of additional energy and NADH by passage through the tricarboxylic acid (TCA) cycle, which is also known as the Krebs or citric acid cycle. In that cycle, NADH is formed which, together with the NADH formed during glycolysis, can yield additional ATP by the passage of the electrons released through an electron transport chain, a process known as oxidative phosphorylation. The electrons released from the oxidation of NADH to NAD pass through a series of alternately oxidized and reduced flavoprotein and iron-containing cytochrome molecules and finally are used to reduce molecular oxygen (a terminal electron acceptor) to water. In a process not as well understood as aerobic metabolism, some anaerobic microorganisms can use nitrate, sulfate, or bicarbonate ions as terminal electron acceptors. Nitrate has been shown to serve as a terminal electron acceptor for the anaerobic biodegradation of benzene, toluene, ethylene, and xylene (BTEX) and lower molecular weight polyaromatic hydrocarbons (PAHs) under denitrifying conditions. Sulfate also has been shown to serve as a terminal electron acceptor for the anaerobic biodegradation of BTEX under sulfate-reducing conditions. The reductive dehalogenation of PCBs, for example, is thought to occur under methanogenic conditions.

In summary, bioremediation is the enhancement of a natural process in a controlled environment for the purpose of improving environmental quality and reducing the risks to human health following the introduction of a toxic, hazardous compound into that environment.

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Background

Paul E. Flathman OHM Remediation Services Corp. Findlay, OH

Objectives

- Introduce concepts and terminology of bioremediation/biodegradation
- Discuss factors that influence biodegradation
- Explore benefits/limitations of bioremediation
- Provide increased comfort level with this technology

Use of Bioremediation Limited by Understanding of:

- Biodegradation processes
- Appropriate applications
- Control and enhancement in environmental matrices
- Remediation costs

Benefits of Bioremediation

- On site
- Natural process
- Residues typically nontoxic
- Environment minimally disturbed
- Typically cost effective compared to excavation followed by incineration and/or landfilling

Bioremediation

Manipulation of living systems to bring about desired chemical and/or physical changes in a confined and regulated environment

Desired Changes

- Decomposition of toxic, hazardous compounds
- Improvement in environmental quality
- Reduction of human health risks

Hybrid of:

- Microbiology
- Engineering
- Soil science
- Ecology
- Hydrogeology
- Toxicology

Biodegradation

 Biological transformation of an organic compound to another form without regard to extent

Mineralization

- Conversion of an organic compound to carbon dioxide, water, methane, and other inorganic forms (e.g., Cl-, NH₄+)
 - Aerobic onditions

 + O₂ → CO₂ + H₂O + Cl⁻ + ATP + Biomass
 - Anaerobic (methanogenic) CH₄ + CO₂ + Cl⁻ + ATP + Biomass

Xenobiotic Compounds

- Compounds foreign to biosphere having been present for an instant on evolutionary time scale
- Can be persistent or recalcitrant compounds

Xenobiotic Compounds (cont.)

- Polychlorinated biphenyls (PCBs)
- Chlorinated pesticides/wood preservatives
 - Pentachlorophenol (PCP)
 - **■** Dioxins
 - **■** Toxaphene

Xenobiotic Compounds (cont.)

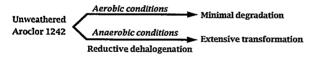
- Chlorinated aliphatics
 - Methylene chloride (dichloromethane, DCM)
 - Tetrachloroethylene (perchloroethylene)
 - 1,1,2,2-Tetrachloroethane
- Munitions
 - **TNT**

Recalcitrant/Refractory Compound

- Compound inherently resistant to any degree of biodegradation
- Compounds so listed continuously change
 - **TCE**
 - **■PCBs**

Persistent Compound

- Compound that fails to undergo biodegradation under a specified set of conditions
- Compound may be inherently biodegradable yet persist in the environment

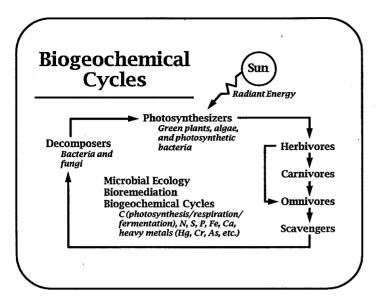


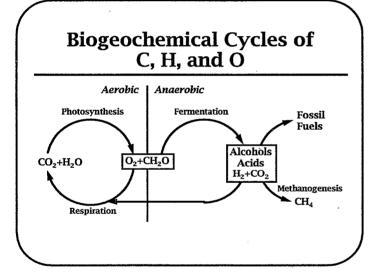
Ecology

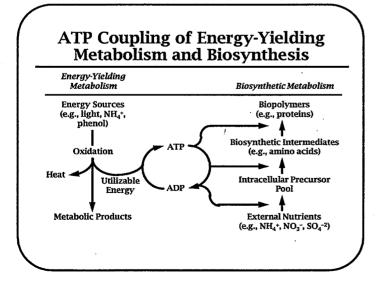
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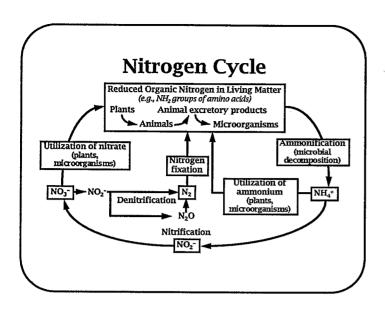
- Oikos-Household or dwelling
- **■***Logos*-Law

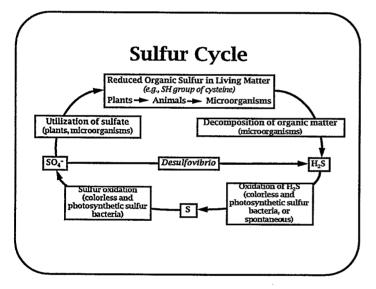
Science that explores interrelationships between organisms and their living and nonliving environments







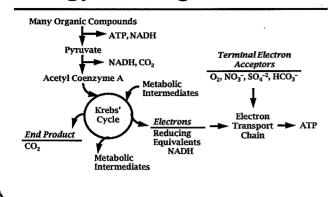




Energy for Growth Energy Source for ATP Generation Chemoautotrophs Nitrifying bacteria and sulfur, iron, and hydrogen-oxidizing bacteria Chemoheterotrophs Fungl and bacteria Preformed Organic Matter (e.g., phenol) Preformed Organic Matter (e.g., phenol)

Sources of Carbon and

Energy-Yielding Metabolism



Energy-Yielding Metabolism (cont.)

I. Fermentation

Organic compounds serve both as electron donors and electron acceptors for the oxidation of substrates

$$C_6H_{12}O_6 \longrightarrow CO_2 + C_2H_5OH + ATP + Biomass$$
 Glucose Ethanol (blood sugar) (grain alcohol)

Energy-Yielding Metabolism (cont.)

- I. Fermentation (continued)
 - **■**O₂ Relationship
 - » Obligate Anaerobes
 - » Facultative Anaerobes
 - On exposure to O₂, most microflora shift to aerobic respiration

Energy-Yielding Metabolism (cont.)

II. Respiration

Organic compounds or reduced inorganic compounds serve as electron donors for the oxidation of substrates

- **■** Aerobic Respiration
 - » O₂ is terminal electron acceptor
 - » H₂O is produced
- Anaerobic Respiration
 - » Denitrification
 - NO₃- (nitrate) is terminal electron acceptor
 - N₂ (nitrogen gas) is produced

Energy-Yielding Metabolism (cont.)

II. Respiration (continued)

- Anaerobic Respiration (continued)
 - » Sulfate Reduction
 - ${ullet}$ SO $_4^{-2}$ (sulfate) is terminal electron acceptor
 - S⁻² (sulfide) is produced (e.g., H₂S, FeS)
 - » Methanogenesis
 - $^{\bullet}$ HCO $_{3}^{-}$ (bicarbonate) is terminal electron acceptor
 - CH₄ (methane, marsh gas) is produced

Requirements for Bioremediation

- Available contaminant (substrate)
- Acceptable temperature
- Electron acceptor
 (O₂, NO₃-, SO₄-2, HCO₃-)
- Nontoxic concentration of contaminant

Requirements for Bioremediation (cont.)

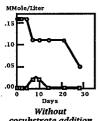
- Available mineral nutrients
- Acceptable pH
- Surfactant if contaminant not water soluble
- Cosubstrate if contaminant cometabolized

Requirements for Bioremediation (cont.)

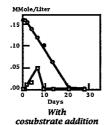
- Primary substrate if contaminant and available TOC present at trace levels
- Hydraulic conductivity >10⁻⁴ cm/sec for in situ subsurface soil/ground water treatment
- Soil moisture content 60 to 80% of soil moisture holding capacity for solid-phase (or land) treatment

Cometabolism/Cooxidation

 Transformation of a nongrowth-supporting substrate in the obligate presence of a growth-supporting substrate (cosubstrate)



cosubstrate addition



Biodegradable Organics

Group I Highly Soluble, Degradable Compounds

- Alcohols— Methanol
- Ethers— Tetrahydrofuran (THF)
- Ketones— Acetone
 Methylethylketone (MEK)
 Methylisobutylketone (MIBK)
- Nitrogenous— Acrylonitrile
- Substituted Benzenes— Isophorone Toluic Acids Chlorobenzenes

Biodegradable Organics (cont.)

Group II

Readily Biodegradable Compounds

- Benzene, Ethylbenzene, Toluene, Xylenes (BETX)
- Virtually All Petroleum Cuts
- Chlorinated Aliphatics-

Methylene Chloride (or Dichloromethane, DCM) Hexachloro-1,3-butadiene

- Naphthalenes— 2-Chloronaphthalene
- Phenols— 2-Chlorophenol
- Phthalates— Diethylphthalate

SITE CHARACTERIZATION REQUIREMENTS

Ronald C. Sims
Utah State University
Logan, UT

INTRODUCTION

An adequate site characterization, including surface soil and subsurface aquifer characteristics, subsurface hydrogeology, type of contaminants present, and the extent and distribution of contamination, is the basis for the rational design of a bioremediation system. Site-specific characteristics can function as constraints that limit the rate and/or the extent of bioremediation of the site. Therefore, a thorough site characterization is necessary to determine both the three-dimensional extent of contamination and engineering constraints and opportunities.

EVALUATION OF EXTENT AND DISTRIBUTION OF CONTAMINATION

Evaluating the extent and distribution of contamination at a site will provide important information that can be used to select specific bioremediation technologies, for example, prepared-bed, bioventing, compost, in situ reactors, above-ground soil slurry reactors, or above-ground water treatment reactors, or to select a treatment train that represents a combination of physical/chemical and biological technologies. Extent of contamination generally is determined through three-dimensional sampling and characterization of the several physical phases present at a site. If contamination is widespread and low in concentration, then in situ treatment might be feasible. Conversely, a high concentration of contaminants present in a vadose zone that is directly sponsoring contaminants to the ground water might require soil excavation and placement in a prepared-bed reactor. Also, sampling the ground water phase at a site to determine extent of contamination is necessary, but not sufficient. A contaminated site is a system generally consisting of four phases: (1) solid, which has two components, an organic matter compartment and an inorganic mineral compartment composed of sand, silt, and clay; (2) oil (commonly referred to as nonaqueous phase liquid, or NAPL), (3) gas, and (4) aqueous (leachate or ground water). Figure 1 shows the phases that need to be characterized with regard to extent and distribution of contamination. Each phase in Figure 1 also can be a site for biological reactions that result in the transformation of a parent chemical and therefore destruction of the parent compound. Each contaminated phase in the subsurface might require a different bioremediation technology to optimize site remediation.

Distribution of contaminants at a site is determined not only by the original placement and escape of contaminants, which can be determined through a three-dimensional sampling program, but also by physical and chemical properties of the contaminants. Physical and chemical properties of contaminants will determine whether contaminants are leachable, volatile, or adsorbable, and therefore will indicate which subsurface phase(s) contain the contaminant(s). Those physical phases containing the contaminants require evaluation of bioremediation potential. When the physical and chemical properties are evaluated within the context of site characteristics, a site-based waste characterization can be used to identify the phases at the site and the chemicals associated with each phase.

MICROORGANISMS

Microbiological characterization of a contaminated site should be conducted to ensure that the site has a viable community of microorganisms to accomplish biodegradation of the organic contaminants present at the site. Soil microorganism groups most commonly involved in bioremediation include bacteria, actinomycetes, and fungi. Approaches for characterizing the kinds, numbers, and metabolic activities of soil microorganisms include (1) determination of the form arrangement and biomass of microorganisms in soil, (2) isolation and characterization of subgroups and species, and (3) detection and measurement of metabolic processes. Generally, information concerning measurement of microbial activity in situ or under conditions designed to simulate field characteristics is more useful than information concerning microbial enumeration (counting), because microbial density within a subsurface system generally is not well correlated with microbial activity within the system.

Examples of techniques to characterize microorganism activity include measurement of ¹⁴CO₂ evolution (mineralization) of spiked radiolabeled parent compound, disappearance of the parent compound and production of metabolic intermediates, and the use of bioassays to measure the toxicity of a contaminated system or subsurface phase (e.g., leachate or ground water) to soil microorganisms or soil enzymes. Microbial enumeration can be accomplished by direct microscopy of soil (e.g., fluorescent staining and buried-slide techniques), biomass measurement by chemical techniques (e.g., measurement of ATP), and cultural counts of microorganisms (e.g., plate counts, dilution counts, isolation of specific organisms).

Microbial ecologists have identified ranges of critical environmental conditions that affect the activity of soil microorganisms (Table 1). Many of these conditions are controllable and can be changed to enhance the biodegradation of organic constituents. A discussion of the factors covered below including principles, status of the technology, secondary impacts, equipment, advantages and disadvantages, and references are provided in U.S. EPA (1990).

OXYGEN PROFILE

With regard to unsaturated soil, microbial respiration, plant root respiration, and respiration of other organisms remove oxygen from the soil atmosphere and enrich it with carbon dioxide. Gases diffuse into the soil from the air above it, and gases in the soil atmosphere diffuse into the air. Oxygen concentration in a soil, however, can be much less than in air while carbon dioxide concentrations in soil can be many times that in air. A large fraction of the microbial population within the soil depends on oxygen as the terminal electron acceptor in metabolism. When soil pores become filled with water, the diffusion of gases through the soil is restricted. Oxygen diffuses

through air 10,000 times faster than it does through water. Oxygen can be consumed faster than it can be replaced by diffusion from the atmosphere, and the soil can become anaerobic. Clay content of soil and the presence of organic matter also can affect oxygen content in soil. Clayey soils tend to retain a higher moisture content, which restricts oxygen diffusion, while organic matter can increase microbial activity and deplete available oxygen. Facultative anaerobic organisms, which can use oxygen when it is present or can switch to alternative electron acceptors such as nitrate or sulfate in the absence of oxygen, and obligate anaerobic organisms become the dominant populations. Additional information concerning in situ anaerobic bioremediation can be found elsewhere (U.S. EPA, 1990).

Oxygen concentrations in soil systems can be increased by tilling and draining unsaturated soil, for example in prepared-bed, compost, and in situ systems. Oxygen concentrations in soil systems also can be increased through the application of bioventing systems, where air is forced through a soil system and carries oxygen to soil microorganisms to accomplish aerobic degradation. Air has a much greater potential than water for delivering oxygen to soil on a weight-to-weight and volume-to-volume basis. Oxygen provided by air is more easily delivered since the fluid is less viscous than water. High oxygen concentrations in air also provide a large driving force for diffusions of oxygen into less permeable areas within a soil formation. Hinchee (1989) and Hinchee and Downey (1990) successfully applied bioventing for enhancement of biodegradation of petroleum hydrocarbons in JP-4 jet fuel contaminated soil at Hill Air Force Base, Ogden, Utah, in increasing subsurface oxygen concentrations. Oxygen and carbon dioxide concentrations were monitored and correlated well with hydrocarbon biodegradation.

Within saturated environments, oxygen transport is considered to be the rate-limiting step in aerobic bioremediation of contaminated hydrocarbons. Oxygen profiles have been used at the Traverse City, Michigan, site contaminated with jet fuel (U.S. EPA, 1991a). Increasing the oxygen concentration in water through addition of hydrogen peroxide (H_2O_2) and enhancing oxygen delivery to the contaminated subsurface through management of hydraulic gradients positively affected the rate of biodegradation of the jet fuel components benzene, toluene, and xylene (BTX). Although high concentrations of H_2O_2 can be toxic to microorganisms, acclimation is possible by slowly increasing the concentration of H_2O_2 with time.

NUTRIENTS

Microbial metabolism and growth are dependent on adequate supplies of essential macroand micronutrients. Required nutrients must be present and available to microorganisms in a
suitable form, appropriate concentrations, and proper ratios. If the wastes present at a site are high
in carbonaceous materials and low in nitrogen (N) and phosphorus (P), the subsurface can become
depleted of available N and P required for biodegradation of the organic contaminants. Addition
of nutrients can be required as a management technique to enhance microbial degradation.
Commercial agricultural fertilizers are available. Power implements, tillers, and applicators can be
used to apply the nutrients to land-based systems, or nutrients can be added to treated water from
a pump-and-treat system and applied through reinfiltration or irrigation (U.S. EPA, 1991b).
Recommended ratios for subsurface systems of carbon (C), N, and P are 120:10:1 on a weight basis.
Examples of sites where nutrients have been added to enhance microbial degradation of hydrocarbon
contaminants include Traverse City (saturated environment in in situ bioremediation) (U.S. EPA,
1991a) and the Champion International Superfund Site in Libby, Montana (Sims et al., 1993). At
the site in Libby, Montana, nutrients are added to enhance bioremediation in a prepared-bed system,

in an above-ground reactor for treating extracted ground water, and in injection wells designed for in situ bioremediation.

MOISTURE

Water is necessary for microbial life, and the soil water matrix potential against which microorganisms must extract water from the soil regulates their activity. The soil matrix potential is the energy required to extract water from the soil pores to overcome capillary and adsorptive forces. Soil water also serves as the transport medium through which many nutrients and organic constituents diffuse to the microbial cell, and through which metabolic waste products are removed. Soil water also affects soil aeration status, nature, and amount of soluble materials; soil water osmotic pressure; and the pH of the soil solution (U.S. EPA, 1989). Generally, microbial activity measured as biodegradation rates and rates of detoxification of contaminants in soil has been found to be highest at soil moisture contents of 60 to 80 percent of field capacity, compared with those of 20 to 40 percent of field capacity (U.S. EPA, 1991a).

Soil moisture can be increased using standard agricultural irrigation practices such as overhead sprinklers or subirrigation. To remove excess water or lower the water table to prevent water-logging, drainage or well point systems can be used. Also, the addition of vegetation to a site will increase evapotranspiration of water and therefore assist in retarding the downward migration of water (i.e., leaching) (U.S. EPA, 1990). Soil moisture control can be combined with pump-and-treat systems where contaminated ground water is extracted, treated to remove contamination, and amended with nutrients and an oxygen source before it is reinfiltrated or used for irrigation (U.S. EPA, 1991b).

ENVIRONMENTAL FACTORS

Environmental factors including pH, redox potential, and temperature are important parameters that will affect the rate and extent of bioremediation in unsaturated and saturated subsurface systems. Outside of the pH range of 5.5 to 8.5, microbial activity is generally decreased. Maintaining soils near neutral pH is most often recommended for enhanced bioremediation (U.S. EPA, 1990). Acidic soils are known to become acclimated to bacteria and fungi over time, however. Soil pH values greater than 6 are recommended for immobilization of metals. Conventional agricultural practices for increasing soil pH include adding lime periodically and mixing the lime with the acidic soil. The amount of lime required to effect a pH change in a particular site/soil/waste system must be determined by a soil-testing laboratory (U.S. EPA, 1990).

Redox potential of a subsurface environment has a large influence on microbial metabolism and activity. For aerobic metabolism, the redox potential should be greater than 50 millivolts; for anaerobic conditions, less than 50 millivolts. A low redox potential provides alternative electron acceptors to oxygen; for example, nitrate, nitrite, iron, manganese, and sulfate can act as electron acceptors. A redox potential higher than 50 millivolts is conducive to biodegradation of hydrocarbons; less than 50 millivolts is conducive to degradation of chlorinated hydrocarbons, and generally less than 35 millivolts (U.S. EPA, 1990) is required.

Soil temperature has an important effect on microbial activity and has been correlated with biodegradation rates of specific organic compounds (U.S. EPA, 1991a). Prepared-bed and in situ bioremediation should be planned to take advantage of the warm season in cooler climates.

Vegetation can act as an insulator against heat loss and limit frost penetration. Application of mulches can help control heat loss at night and heat gain during the day (U.S. EPA, 1991a; 1990).

SUMMARY AND SOURCES OF ADDITIONAL INFORMATION

An adequate site characterization, including the contaminant distribution as influenced by site geology and hydrogeology and chemical properties, is the basis for the rational design of a bioremediation system. Site characterization information assists in the identification of specific physical phases requiring remediation. Site-specific characteristics can function as constraints that limit the rate and/or the extent of bioremediation of the site. Information concerning microorganism activity, oxygen profiles, nutrients, moisture, and environmental conditions including pH, redox potential, and temperature are necessary for selecting bioremediation techniques, and for selecting treatment trains that combine physical/chemical treatments with biological treatment.

Additional information concerning practical aspects of site characterization for bioremediation of contaminated ground water is available in Sims et al. (1992).

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Table 1. Critical Environmental Factors for Soil Microbial Activity

Environmental Factor	Optimum Levels
Oxygen	Aerobic metabolism: greater than 0.2 mg/L dissolved oxygen, minimum air-filled pore space of 10% ; Anaerobic metabolism: less than 0.2 mg/L dissolved oxygen, O_2 concentration less than 1% air-filled pore space.
Nutrients	Sufficient nitrogen, phosphorus, and other nutrients so not limiting microbial growth (suggested C:N:P ratio of 120:10:1)
Moisture	Unsaturated soil: 25-85% of water holding capacity; -0.01 MPa; will affect oxygen transfer into soil (aerobic status) In saturated zone, water will affect transport rate of oxygen, and therefore will affect rate of aerobic remediation
Environment (pH)	5.5 - 8.5
Environment (Redox)	Aerobes and facultative anaerobes: greater than 50 millivolts; Anaerobes: less than 50 millivolts
Environment (Temperature)	15 - 45 C (mesophilic)
Source: U.S. EPA (1989).	

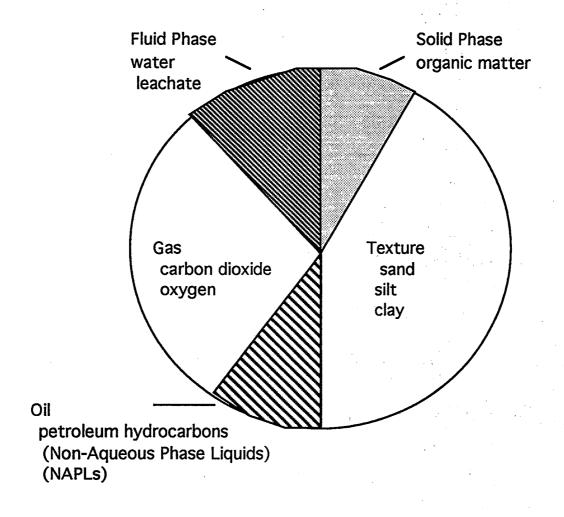
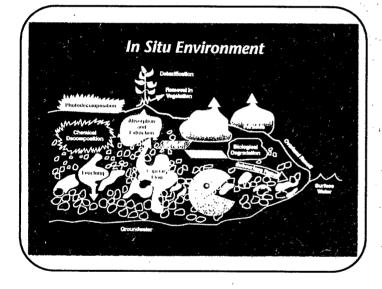
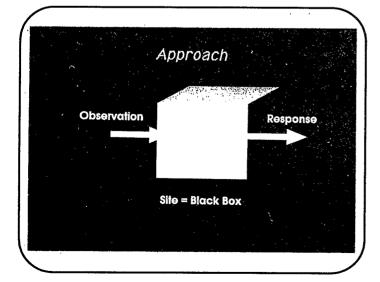


Figure 1. Phases for characterization and for evaluation of bioremediation at each site (U.S. EPA, 1991).

Site Characterization Requirements

Ronald C. Sims Utah State University Logan, UT





Site Characterization Requirements

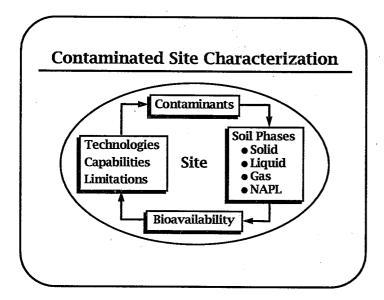
- Evaluation of Extent and Distribution of Contamination
- Microorganisms
- Oxygen Profile
- Nutrients
- Moisture
- Environmental Factors

Critical Environmental Factors for Soil Microbial Activity

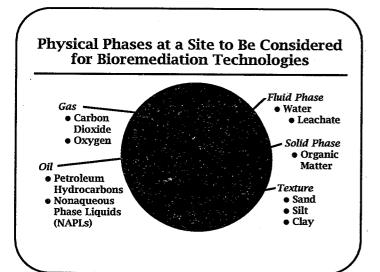
Environmental Factor	Effects
Oxygen	Metabolism: Aerobic/Anaerobic Degradation Pathways
Nutrients	Nitrogen, Phosphorus Activity
Moisture	Unsaturated/Saturated Soil Oxygen Transfer

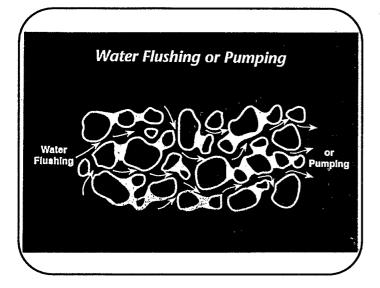
Critical Environmental Factors for Soil Microbial Activity

Environmental Factor	Effects
Environment	5.5-8.5
(pH)	Activity
Environment (Redox)	Aerobes/Facultative Anaerobes: >50 mV Anaerobes: <50 mV Degradation Pathways
Environment	15-45°C (Mesophilic)
(Temperature)	Activity

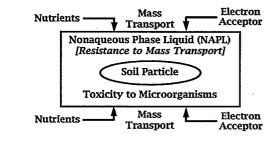


Evaluation of Extent and Distribution of Contamination

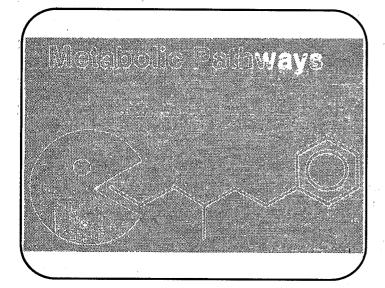




Mass Transport and Toxicity Limitations to Biological Treatment of Soils as a Function of NAPL Concentration



Microorganisms

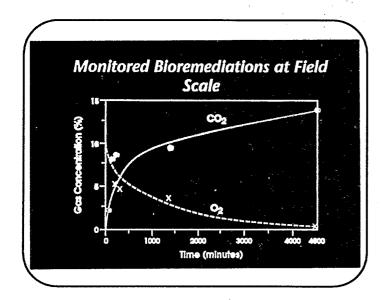


Soil Microorganisms

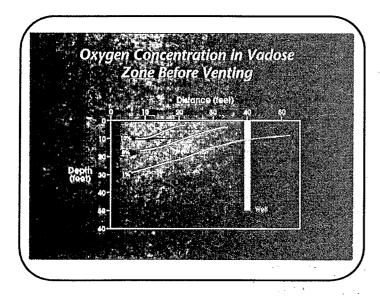
- Bacteria
- Actinomycetes
- **●Fungi**

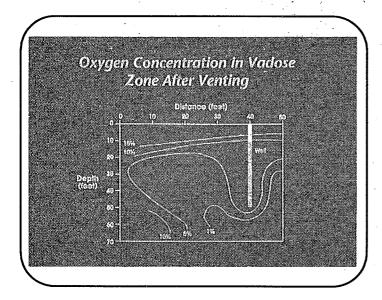
Soil Microorganisms

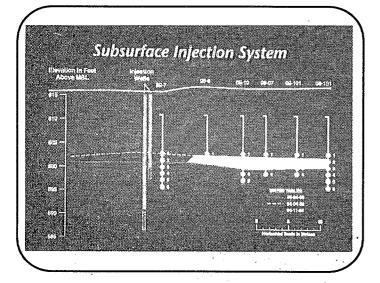
- Enumeration
- Identification
- •Relationship of Population Size (Numbers Per Gram of Soil) to Activity Is Not Well Established



Oxygen Profile



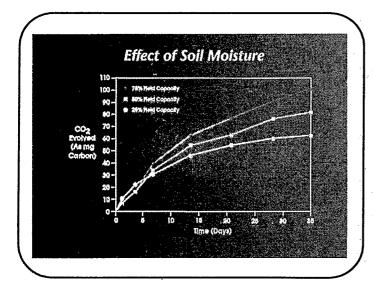


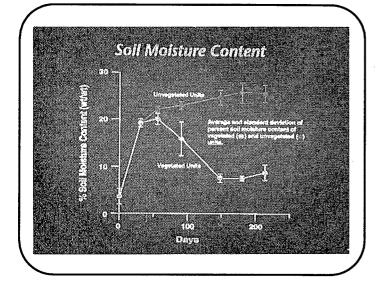


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Fe+2 (mg/L)	Mn+2 (mg/L)
ND	0.7 ND
ND N	1 0
ND	ND
ND	ND
1.2	6.0
ND	0.6
ND	0.6 0.5
2.0	2.7
	(mg/L) ND ND ND ND ND ND 1.2

Nutrients

Moisture



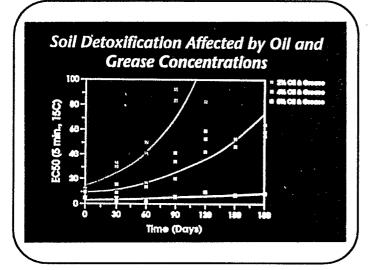


Environmental Factors

Aerobic Biodegradation – Respiration $C_6H_6+7\%O_2 \longrightarrow 6 CO_2+3 H_2O$ $3.1 lb O_2/lb C_6H_6$ $C_6H_{14}+9\%O_2 \longrightarrow 6 CO_2+7 H_2O$ $3.5_2lb O_2/lb C_6H_{14}$

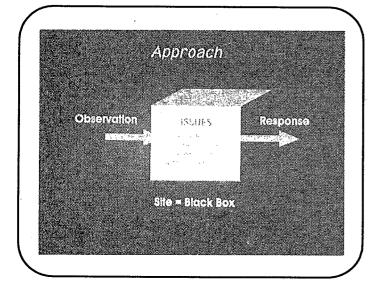
Oxygen Supply

Oxygen Diffuses through Water at a Rate That Is 10,000 Times Less Than the Rate at Which Oxygen Diffuses through Air



Redox and Biodegradation

- Maximum rate of degradation often correlated with continuous supply of oxygen
- Degradation may result in anaerobic conditions (i.e., lower redox potential)
- Degradative pathways for some chemicals occur under reducing conditions (e.g., reductive dechlorination)



SOIL TREATMENT FACTORS • TOXICITY TO MICROORGANISM • CHEMICAL • DOSE • MASS TRANSFER TO MICROORGANISM • NUTRIENTS • OXYGEN • CHEMICAL

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TREATABILITY STUDIES

John Rogers
U.S. Environmental Protection Agency
Athens, GA

and

P. Hap Pritchard
U.S. Environmental Protection Agency
Gulf Breeze, FL

and

Paul Flathman
OHM Remediation Services Corporation
Findlay, OH

INTRODUCTION

Because of the tight time constraints in effecting the cleanup of Superfund hazardous waste sites, making timely decisions in selecting the appropriate remediation technology is imperative. Such decisions, however, should be predicated on sound information about the site and some initial information about the individual remediation processes. Information on the site can be obtained from the initial site characterization. Information about the remediation process can be obtained from published literature as well as from simple laboratory feasibility studies. The purpose of this presentation is to describe what information should be collected during the initial site characterization to evaluate bioremediation processes and also to describe some simple feasibility studies that can be used to assist in the selection process.

At all sites, an initial site investigation is conducted to establish the identity of chemicals at the site, determine the nature and extent of the contamination, obtain a description of the environmental characteristics of the site, and make an initial appraisal of the appropriate remediation technologies. This information is used to determine if the site is hazardous and, if necessary, what action should be taken to reduce the hazards to a safe level. The amount of information required to make these decisions is significant. This presentation and these handouts emphasize only the information that is required to evaluate bioremediation.

The first step is to define the problem and identify the types of contaminants. The physical and chemical properties of the compounds that can influence biodegradation are identified and the literature is assessed for information concerning the degradation of the compounds.

A second area of activity involves determining the distribution of the chemicals within the site. Examples of specific analytical procedures are presented in Appendix A. In this stage, the site is divided into a series of subsites for further evaluation. Compound concentration becomes important at this point, because concentrations might be toxic and some pretreatment might be required before bioremediation can be considered. Pretreatment might consist of dilution of the contaminated area, for example, by mixing of wastes.

A third area involves characterization of the contaminated environment. This characterization extends from gross characteristics such as soil, sediment, water, or subsurface material to more specific characteristics such as permeability, redox conditions, pH, and hydrology. The microbiological characteristics of the different environments also are identified. For example, anaerobic bacteria would predominate in sediments whereas aerobic organisms would predominate in unsaturated soils.

In a fourth area, any adjustment of the environment that might be required to permit bioremediation is addressed directly. Such adjustments could include altering pH, preremoving toxic metals, and changing moisture content. In some cases, bioremediation might not be judged as a possible option because the environment cannot be adjusted.

A fifth area involves evaluation of the microbiological needs of the site. In this area, the concern becomes the availability of nutrients, the potential additions of bacteria with specific degradative characteristics, and whether the process should be conducted under anaerobic or aerobic conditions.

In a sixth area, a feasibility study is designed to test-potential bioremediation scenarios.

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APPENDIX A

CHEMICAL ANALYSIS OF TEST CHEMICALS AND/OR WASTE SAMPLES

The selection of a suitable extraction procedure for a given combination of analyte(s) and soil matrix generally requires some method development (Coover et al., 1987). For example, methods that successfully recover a compound from one medium might not adequately recover the same chemical from similar media (Albro, 1979). Also, extraction recoveries from a given set of structurally similar media might vary (Albro, 1979).

Where possible, it is recommended that the existing and established analytical methods described in Test Methods for Evaluating Solid Waste (USEPA SW-846 3rd Edition November 1986) be used.

The recommended SW-846 methodology for selected analytes are:

Gas Phase Volatiles

Method 0010	Modified Method 5 Sampling Train
Method 0020	Source Assessment Sampling System (SSAS)
Method 0030	Volatile Organic Sampling Train (VOST)
Method 5040	Protocol for Analysis of Sorbent Cartridges from Volatile Organic Sampling
	Train.

Soil Phase Volatiles

Method 5030	Purge and Trap
Method 8010	Halogenated Volatile Organics
Method 8015	Nonhalogenated Volatile Organics
	Aromatic Volatile Organics
Method 8030	Acrolein, Acrylonitrile, Acetonitrile

Selected Nonvolatiles

Method 8040	Phenols
Method 8060	Phthalate Esters
Method 8080	Organic Pesticides and PCBs
Method 8090	Nitroaromatics
Method 8100	Polynuclear Aromatic Hydrocarbons
Method 8120	Chlorinated Hydrocarbons
Method 8140	Organophosphorous Pesticides
Method 8150	Chlorinated Herbicides

Recommended extraction/concentration techniques (soils and sediments) are:

Method 3540	Soxhlet Extraction
Method 3550	Sonication Extraction

Other published methods for Soxhlet extraction (Anderson et al., 1985; Bossert et al., 1984; Coover et al., 1987; Eiceman et al., 1986; Kjolholt, 1985; Grimalt et al., 1986), sonication extraction (de Leevw et al., 1986; Sims, 1982) and homogenization and extraction (Coover et al., 1987; Fowlie and Bulman, 1986; Lopez-Avila et al., 1983; Sims, 1982; Stott and Tabatabai, 1983; and U.S. EPA, 1982a) and extraction of materials from treatability studies (Brunner et al., 1985; Russell and McDuffie, 1983) are available for reference and special applications.

Soil spiking and recovery studies should be conducted to determine the effects of soil, test substance(s), and soil test substance(s) matrix on chemical extraction and recovery efficiency. Soil samples should be sterilized using a method such as mercuric chloride, causing minimal change in soil physical and chemical properties (Fowlie and Bulman, 1986). The sterile soil should be spiked with the test substance(s) to achieve a range of initial oil concentrations (Coover et al., 1987). The range of concentration should include the highest concentration and less than one-half of the lowest initial concentration to be used in degradation evaluations. Extractions of the soil/test-substance(s) mixtures using the selected procedure will allow the evaluation of the effect of test substance(s) soil concentrations on recovery efficiency. The effect of soil concentration was evaluated and found to be significant for anthracene and benzo(a) pyrene by Fowlie and Bulman (1986).

Extracts of the soil and complex wastes should be spiked with test substance(s) of interest to evaluate the effect of these matrices on chemical identification and quantification. Interferences due to the extract matrix might be identified. Extraction procedures or instrumentation used for identification and quantification then can be changed if necessary.

Standard curves should be prepared using primary standards of the test substance(s), or chemicals in the test substance(s), dissolved in a suitable solvent that does not interfere with chemical identification and quantification. Standard curves should be generated using at least six points ranging from the highest concentration anticipated to the detection limit for the chemical.

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Treatability Studies

John Rogers
Athens Environmental Research Laboratory
U.S. Environmental Protection Agency
Athens, GA

MINIMUM REQUIREMENTS FOR QA/QC

- Project description
- Project organization
- QA objectives
- Sample custody
- Internal QC checks
- Performance and system audits
- Preventative maintenance schedule

MINIMUM REQUIREMENTS FOR QA/QC (Continued)

- ◆ Data assessment procedures
- Corrective actions
- QA reports
- Sampling plan

DOCUMENTATION REQUIREMENTS FOR QA

- Accepted sampling techniques
- ◆ Field actions contrary to QAPP
- All pre-field activities
- QC for field measurement data
- Field activities
- Post-field activities
- Quality control samples (generation & use)

QA FOR ANALYTICAL PROCEDURES

- Duplicate spike
- Reagent blank
- Documentation of fill samples
- Analytical procedures for surrogate compounds
- Recovery efficiency for columns
- Detection limits and data reduction

QA FOR ANALYTICAL PROCEDURES (Continued)

- Internal QC checks
- Performance and system audits
- Equipment calibration
- Extraction and sample preparation procedures

SITE CHARACTERIZATION

- Description of facility
- Identification of contaminants
- Extent of contamination

DESCRIPTION OF FACILITY

- Geographic location, property lines, topography and surface drainage
- Infrastructure present
- Description of hazardous waste treatment, storage, disposal and spill areas
- Surrounding land uses
- Production and groundwater monitoring wells

IDENTIFICATION OF CONTAMINANTS

- Organic/inorganic
- Chemical classes (metals, halogenated volatiles, pesticides)
- Mixtures

INITIAL MATERIAL CHARACTERIZATION

- ◆ Organics: GC or GC/MS, HPLC
- Group analysis: priority pollutants. fuels analysis, EP-Toxicity
- Metals: AA, ICP
- General chemistry: TOC, COD, BOD, TPH, Oil & Grease (IR or GC), TKN, NO₃, TP, PO₄, SO₄
- Optional radioisotope analysis: isotopically labeled substrate studies, 14CO₂

GENERAL CHEMISTRY

Analysis	Price Per Sample
Total Organic Carbon (TOC)	40 ·
Total Kjeldahl Nitrogen (TKN)	50
Chromium VI	25
Cyanides	50
Phenols	50
Orthophoshates	20
Total Phosphorous	35
Nitrate	20
Sulfide	25
Oil and Grease	40
Total Suspended Solids (TSS)	15
Chemical Oxygen Demand (COD)	35
Ion Chromography	65
. (Bromide, Chloride, Fluoride, Nitrate,	
Nitrite, Phosphate, Sulfate)	
Microtox	Price on Request
Radio Isotope Analysis (Liquid Scintillation)	

ORGANICS				
Analysis	Price Fo	or Sample Solids	Method Water	Number Solid:
GC/MS			•	
Volatile Organic Analysis	240	280	624	8240
Acid/Base Neutrals	420	475	625	8270
Confirmation by GC/MS	100	150	023	0270
GC				
Pesticides/PCBs	150	200	608	0000
PCBs in Oil	50	200	600	8080
Herbicides	200	. 250		8150
Pheno1 s	100	100	604	8040
Pentachlorophenol (PCP)	90	90	604	00.10
Polynuclear Aromatic			•	
Hydrocarbons (PNA)	115	130	610	8100
Hydrocarbon Fuels				_
(gasoline/diesel)	110	130		
Creosote	90	90		

GROUP ANALYSES			
Analysis Priority Pollutants Acid/Base Heutrals (37) Volatile Organic Analysis (31) Pesticides & PCBs (28) Hetals (13)	Price Pe Hater 1195		
Cyanides Phenols	450	450	
EP-Toxicity Sample Prep and Extraction Hetals (Ag. As. Ba. Cd. Hg. Pb. Se) Herbicides and Pesticides (2.4-D. 2.4.5-TP, Endrin, Lindane, Hethoxy Chlor, Toxaphane)			
Fuels Analysis BTX (Benzene, Toluene, Xylene) EDS (Ethyl Dibromide) Tetraethyl Lead (total)	90 100 35	100 120 35	
Characterization of Fuels by GC (Gasoline and Diesel)	110	130	

HETALS		
Hethod of Analysis Graphite Furnance ALS Hydride Cold Vasor	Price	Per Element 20 13 30 30
ICP Multi Element Analysis (Ag. Al. B. Ba. Be. Ca. Cd Co. Cr. Cu. Fe. K. Mg. Mn. Mo. Ma. Mi. Pb. Se. Si. Sn Il. V. 20)	Price	Per Sample
I-12 Elements 13-24 Elements		90 115
Sample Preparation	Price Per Sampl	
Hater Soll/Hater/Sludge EP-Tox Extraction		14 20 95
Group Hetal Analysis Priority Pollutant Hetals (Ag, As, Ba, Cd, Cr, Co, Hg Ml, Pb, Sb, Se, Ti, Zh)	Price P Hater 160	er Sample Solids 199
RCRA Netals Analysis	130	130
(Ag. As, Bs, Cd, Cr. Ng. Fe. Se) Nazardous Substance Listed Hetals (Non CLP) (Ag. Al. As, Ba, Be, Ca, Cd, Co, Cr. Cu. Fe. Ng. K, Mg. Mn, Na, Ni, Pb, Sb, Se, Tl, V, Za	200	215

EXTENT OF CONTAMINATION

- Groundwater
 - Plume size and movement Contaminant concentration profiles
- Soil contamination
 Distribution and concentration
- Surface water contamination
 Horizontal and vertical distribution
- Sediment contamination
 Horizontal and vertical distribution

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PROPERTIES OF CONTAMINANTS

Physical/Chemical Characteristics

- Solid, liquid or gas
- Powder, oily sludge
- Acid, base, valence or oxidation state
- Molecular weight
- Density
- Boiling point

PROPERTIES OF CONTAMINANTS

Physical/Chemical Characteristics (Continued)

- Viscosity
- Solubility in water
- Cohesiveness
- Vapor pressure
- Flash point

PROPERTIES OF CONTAMINANTS Safety Considerations

- Toxicity (human, microorganisms)
- Flammability
- Reactivity
- Corrosiveness
- Oxidizing or reducing characteristics

PROPERTIES OF CONTAMINANTS

Environmental Fate Characteristics

- Sorption
- Biodegradability
- Photodegradability
- Hydrolysis
- Chemical transformation

ENVIRONMENTAL CHARACTERISTICS OF THE SITE

Groundwater

- Flow characteristics
- Hydrogeological units
- Water level and movement
- Man-made influences

ENVIRONMENTAL CHARACTERISTICS OF THE SITE Surface Water And Sediments

- Physical characteristics (location, velocity, depth, surface area, etc.)
- Seasonal fluctuations
- Temperature stratification
- Flooding tendencies
- Drainage patterns
- Evapotranspiration
- End use of water

ENVIRONMENTAL CHARACTERISTICS OF THE SITE

Water/Sediment Chemistry

- Ha •
- Total dissolved solids
- Biological oxygen demand
- Alkalinity
- Conductivity

ENVIRONMENTAL CHARACTERISTICS OF THE SITE

Water/Sediment Chemistry (Continued)

- Dissolved oxygen profiles
- Nutrients NH₃, NO₃/NO₂ PO₄³
- Chemical oxygen demand
- Total organic carbon

ENVIRONMENTAL CHARACTERISTICS OF THE SITE

Distribution And Soil Structure

- SCS soil classification
- Surface soil distribution
- Soil profile ASTM classification
- Depth to water table

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ENVIRONMENTAL CHARACTERISTICS OF THE SITE

Physical Characteristics Of Soils

- Hydraulic conductivity
- Relative permeability
- Bulk density
- Porosity
- Particle size distribution
- Moisture content
- Infiltration
- Vertical flow

ENVIRONMENTAL CHARACTERISTICS OF THE SITE

Chemical Characteristics Of Soils

- Soil stratigraphy
- Soil sorptive capacity
- Ion exchange capacity
- Soil organic content
- Soil pH
- Mineral content

TREATABILITY PROTOCOLS Properties Assessed

- Biodegradability of contaminants
 - -aerobic
 - _anaerobic
- Effectiveness of nutrient amendments
 - -inorganic supplements (N.P.S.)
 - -electron acceptors
 - -organic supplements

TREATABILITY PROTOCOLS

Properties Assessed (Continued)

- Effectiveness of inocula
 - -cultures of natural organisms
 - -specific degraders
- Nondegradative losses
 - -volatilization
 - -sorption
 - -leaching
- Genotoxicity of the waste

PROTOCOL COMPONENTS

- Scope and approach
- Summary and method
- Collection and sampling of site materials
 - sample selection
 - sample collection
 - sample characterization
 - sample transportation
 - sample preservation
 - sample holding times

PROTOCOL COMPONENTS

(Continued)

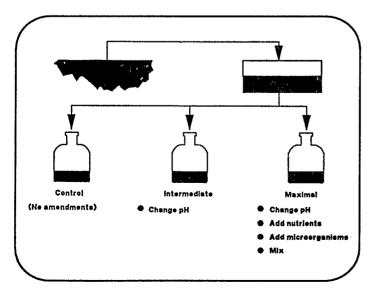
- Apparatus and materials
 - reactor components
 - reactor design
- Procedures
 - reactor setup
 - reactor operation
 - analysis of reactor contents
 - reactor configurations minimal treatment intermediate treatments complete treatment

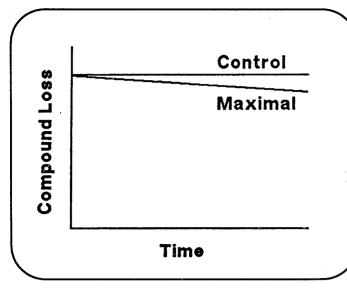
PROTOCOL COMPONENTS (Continued)

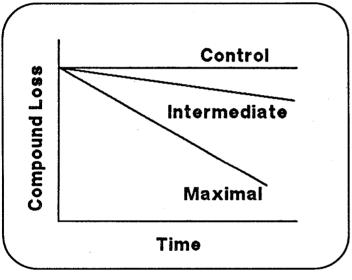
- Data recording and analysis
 - data to be reported
 - determination of degradation rates
- References
 - general
 - chemical analysis
 - sampling

REPRESENTATIVE FIELD SAMPLES REQUIRED FOR BIOTREATABILITY STUDIES

- Evaluation of many samples to obtain a bioactivity site matrix
- Field composite to define any site bioactivity
- Field background samples essential for material characterization





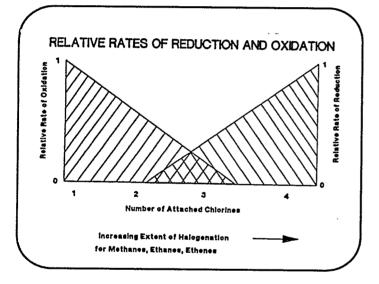


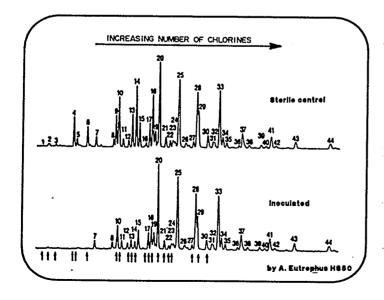
EXPERIMENTAL DESIGN

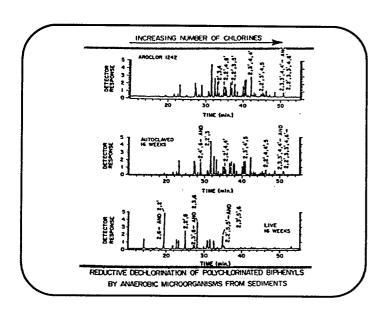
- Controls: sterile, no treatment, field background, number?
- Replicates: duplicate or triplicate? all time points? all controls?
- Treatments: what are the questions you want answered?
- How are you going to optimize the degradation process?

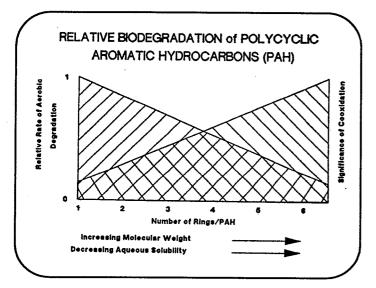
EXPERIMENTAL DESIGN (Continued)

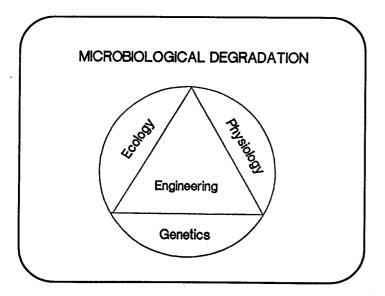
- Treatment time: how long should the study be performed?
- Types of analysis: bulk measurements? waste specific?
- Data reduction: raw data? massaged data? QC/QA?
- Cost considerations: how will it limit scope of test?











FATE OF POLYNUCLEAR AROMATIC CONTAMINATES IN CREOSOTE WASTE DURING LAND TREATMENT 4 Month Study

PNA Class	% Reduction	Half-Life
2 Ring Structure (Naphthalene)	90	33 Days
3 Ring Structure (Phenaphthalene)	80	47 Days
4 Ring Structure (Pyrene)	25	235 Days
Total PNA	65	100 Days

PHYSIOLOGICAL BARRIERS TO BIODEGRADATION

A contaminate will be a poor substrate if:

No active microorganism is present, therefore, no available enzymatic machinery

Microorganisms present, but...

- * Substrate is a poor inducer
- * Substrate concentration is too low
- * Substrate fails to enter cells
- * Cell lacks essential nutrients
- Inhibition/toxicity of enzymes by substrate or products
- * Other necessary microbes are absent

ENVIRONMENTAL BARRIERS TO BIODEGRADATION Potentially Limiting Environmental Factors

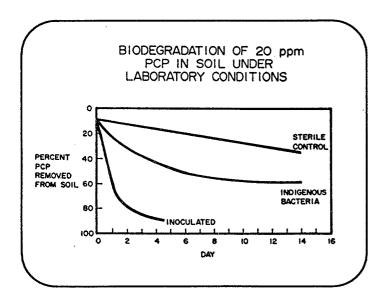
- **♦** pH
- Salinity
- Other synthetic chemicals
- Heavy metals
- Osmotic pressure
- Hydrostatic pressure
- Free water limitations
- Radiation

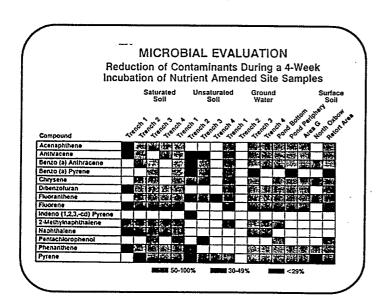
GENETIC BARRIERS TO BIODEGRADATION

- No genetic coding for contaminant degradation
- No genetic coding for transport into ceil
- Genetics for biodegradation exist but not inducible or disbursed on genome
- Low level of expression

BIODEGRADATIONRequires

- Suitable electron acceptor
- Organic substrate
- Nutrients: nitrogen, phosphorous, others
- Trace metals





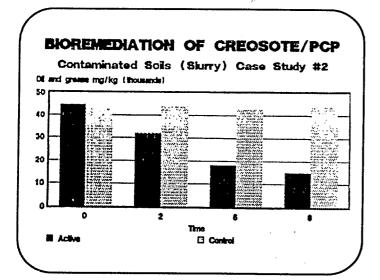
COST BREAKDOWN CASE # 1

X 2	Field Samples Replicates
34 X . 2	Sample Times (0, 4 weeks)
68 X \$ 450	Samples for Analysis GC/MS BNA
\$30,600 + 4,000	Analytical Costs Materials/Labor for Set up

\$34,600 Total Cost (est)*

'Note: No Administrative Charges; Data Evaluation;

Report Preparation; QA/QC



BIOREMEDIATION OF CREOSOTE/PCP Contaminated Soils (Siurry) Case Study #2 mg/kg scil 500 400 300 200 100 Time E Active PNA E Active PCP

CASE STUDY # 2

1 Single Soil Sample

3 Replicates

x2 Treatments (Active Amended/Control)

x4 Sample Times (0,2,6,8 wks)

24 Samples \$ 40 Oil/Grease (T.R.) \$960

x3 (0,4,8 wks) 18 Samples

x\$450 GC/MS(BNA)

\$8100

\$960 + \$8100 = \$9060 Analytical Costs for Experimental Section Initial Material Characterization: TOC, TKN, O-PO₄, NO₃, NH₃

CASE STUDY # 2

(continued)

170

x 2 Replicates

\$340

\$9,400 Total Analytical Costs

\$4,500 Labor/Materials

\$13,900 Total Cost of Treatability*

* Note: No administrative charges; data evaluation, report preparation, QC/QA.

EFFECT OF SLURRY TREATMENT ON PAH AND PCP CONCENTRATIONS^a IN CREOSOTE/PCP **CONTAMINATED SOILS**

Compound	Initial Concentration (mg/kg)	4 Weeks (mg/kg)	8 Weeks (mg/kg)
Acenaphthene	80±12	3.8 ^W	3.8 ^W
Acenaphthalene	3.4±0.1	0.8 ± 0.1	2.1 ^J
Dibenzofuran	17±3	3.8 ^W	3.8 ^W
Fluorene	37±6	3.8 ^W	3.8 ^W
Fluoranthene	167±38	3.9±0.8	3.6±0.3
Anthracene	30±3.5	2.2±0.6	6.7±1.2

EFFECT OF SLURRY TREATMENT ON PAH AND PCP CONCENTRATIONS® IN CREOSOTE/PCP **CONTAMINATED SOILS (Continued)**

Compound	Initial Concentration (mg/kg)	` 4 Weeks (mg/kg)	, 8 Weeks (mg/kg)
Phenanthrene	130±17	0.5±0.1	0.7±0.1
Pyrene	177±38	26±18	10.6±1.5
Chrysene	40±3	5.9±1.1	3.5 ^J
Benzo[a]anthracen	e 34±3	1.7±0.2	1.9±0.2
Benzo[a]pyrene	19±1.3	9.8±1.3	10.6±2.1
Pentachlorophenol		24±2.0	31.6±5.0

PARAMETERS MONITORED DURING THE PILOT TEST OPERATION

Parameter .

Range

Soil temperature

54 F to 82 F

Soil pH

7.0 to 8.9

Soil moisture content

11% to 14% by weight

^{*} Average of triplicate analysis ± variance.

Windetected at the noted concentration.

Satisfies doncentration. Sample data was less than the quantitation limit but greater than zero.

Average of tripiicate analysis ± variance.

Wundetected at the noted concentration.

Estimated concentration, Sample data was less than the quantitation limit but greater than zero.

	Sample		Ve	ek .	
Ireatment	Bunker			_4_	8
CONTROL	1	510,000	410,009	510,000	530,000
	2	470,000	440,000	550,000	510,000
	3	460,000	450,000	510,000	460,000
Average		450,000	433,333	523,333	500,000
Standard Deviation		26,458	20,817	23,094	36,056
5% LOADING RATE	,	33,000	34,000	35,000	30,000
	2	33,000	26,000	28,000	32,000
	3	26,000	31,000	34,000	30,000
Average		30,667	30,333	32,333	30,667
Standard Deviation		4,041	4,041	3,786	1,155
5% LOADING RATE AND					
MUTRIENT-ADJUSTED	3	38,000	18,000	18,000	14.000
	2	43,000	19,000	18,000	16,000
	3	22,000	16,000	22,000	15,000
Average		34,333	17,667	19,333	15,000
Standard Deviation		10,970	1,528	2,309	1,000
S% LOADING RATE,					
MUTRIENT-ADJUSTED	1	22,000	26,000	37,000	18,000
ANG INOCULATED	2	26,000	26,000	29,000	25,000
	3	28,000	59,000	27,000	18,000
Average		25,333	37,000	29,000	20,333
Standard Deviation		3,055	19,053	8,000	4,041
10% LOADING RATE	1	47,000	47,000	41,000	42,000
	2	66,000	87,000	43,000	31,000
	3	46,000	56,000	48,000	34,000
Average		53,000	63,333	44,000	35,667
Standard Deviation		11,269	20,984	3,606	5,686

TOTAL OIL AND GREASE CONCENTRATIONS (mg/kg) IN SOIL MICROCOSHS SIMULATING SOLID PHASE BIOREMEDIATION OF SLUDGE MATERIAL

	Time (weeks)			
Treatment Control	0 480,000	433,333	4 523,333	500,000
5% Loading Rate +pH Adjust	30,667	30,333	32,333	30,667
5% Loading Rate + Nutrients + pH Adjust	34,333	17,667	19,333	15,000
5% Loading Rate + Nutrients + pH Adjust + Inoculated	25,333	37,000	29,000	20,333
10% Loading Rate + Nutrients + pH Adjust	53,000	63,333	44,000	35,667

SUMMARY

- Clearly define the scope of work
- Look for well controlled studies
- Look for statistically valid experimental design
- Always look at the raw data and formulate your own opinion
- Beware of the limitations of standard methodologies
- Always seek expert opinion and independent evaluation

SCALE-UP AND DESIGN ISSUES AND CLEANUP OBJECTIVES

Ronald J. Hicks Groundwater Technology, Inc. Concord, CA

INTRODUCTION

Bioremediation is gaining national and international recognition as a viable treatment technology for remediating contaminated soils and ground water. Increasingly, regulatory agencies at the federal, state, and local level are encouraging the use of this technology. The popularity of bioremediation primarily is due to the potential advantages it offers over traditional treatment technologies such as pump and treat, excavation and disposal, or excavation and incineration.

Bioremediation, however, is not a panacea for solving all of our society's environmental problems. The selection and successful implementation of bioremediation is site specific and depends on a number of physicochemical, hydrogeological, and microbiological factors that determine, not only the efficacy of the technology (i.e., the capacity to bring about the desired change), but also its applicability.

The essence of Total Quality Management is to ensure that the right activity is performed in the right way. Translating this approach to bioremediation (or any remediation technology) means first selecting the proper technology and, second, ensuring that the chosen technology is installed properly.

DOING THE RIGHT THING

The key issues in determining the right thing to do are (1) understanding completely the problem to be addressed, (2) defining the goals, and (3) selecting the proper technology.

Understanding the problem requires a thorough assessment of the site, in terms of its physical, chemical, and microbiological properties; the contaminant, in terms of its mass and treatability; public health and safety issues; and regulatory issues. Defining the goals of remediation in terms of cleanup levels as well as cost and time constraints is essential in properly selecting the technology most appropriate to the site.

Selecting the most appropriate technology for a given site depends primarily on issues of mobility and reactivity.

Mobility refers not only to the chemical, physical, and hydrogeological properties governing the transport of the contaminant, nutrients, and/or oxygen, but also the site conditions and regulatory factors that can affect the movement of the contaminated matrix.

Reactivity refers not only to the biodegradability of the contaminant but also to the interactions between the physical and chemical features of the environment and the contaminant or proposed amendments.

DOING THINGS RIGHT

Once bioremediation has been selected based on feasibility, and a determination of the appropriate bioremediation option has been made, the project manager or operator needs to gather site information relative to the design and implementation of the chosen bioremediation option.

The principal informational needs for design and implementation are those that relate to (1) control of contaminants, (2) mass transport of amendments, (3) monitoring system performance and success, (4) treatment of by-products, and (5) closure of the site.

Control of Contaminant

Gaining hydraulic control of the site to reduce or eliminate migration of the contaminant is necessary for all remediation options where ground water is the contaminated matrix. It is particularly important, however, for in situ bioremediation because of the need to control both the contaminant and amendments to keep both in the zone of treatment.

Mass Transport of Amendments

In most situations, the design and successful implementation of bioremediation is limited by the mass transfer of nutrients and oxygen. Although contaminant concentration is often the only information available, it is essential to determine the approximate mass of the contaminant that is present at the site. One needs to remember that it is a total mass of contaminant that is being remediated, not a concentration. Mass of contaminant is necessary to calculate the length of time required to remediate the site, the total nutrient and oxygen load that will be required, and the costs of remediation. In addition, mass balance of contaminant is probably the best indicator of when a site is near closure.

For bioremediation, not only is the mass of the particular contaminant important, but also the mass of total utilizable organic carbon present. The total mass of utilizable organic carbon ultimately will determine nutrient and oxygen requirements and time of remediation. In unsaturated soils, oxygen most often is supplied by either positive or negative induction of air. For most soil types, this can be accomplished via vapor extraction systems. These systems were designed primarily for the extraction of volatile hydrocarbons; they are extremely effective in supplying oxygen for aerobic biodegradation, however, and often are used for that purpose exclusively. By monitoring carbon dioxide evolution from these systems, increased biological activity can be demonstrated.

Soil permeability is an important determinant of whether or not in situ bioremediation is applicable or if excavation and aboveground treatment is necessary. Low permeabilities generally indicate that the mass transfer of both oxygen and nutrients might be severely impeded and, thus, aboveground bioremediation, in either reactors or biopiles, might be more applicable than in situ bioremediation.

The mass transfer of inorganic nutrients in unsaturated environments usually is accomplished by infiltration of nutrient solutions through the soil. The main limitations to supplying nutrients in this manner are the depth to which the nutrients need to penetrate and the adsorptive capacity of the soil for the nutrients. If the addition of inorganic nutrients in solution form is deemed inappropriate for the particular site, then alternatives, such as supplying the nutrients in a gaseous form, might be more conducive to bioremediation.

As with unsaturated systems, the mass transfer of inorganic nutrients in saturated systems is limited by the adsorptive capacity of the solid matrix. In addition, the hydraulic conductivity might limit the rate of transfer of inorganic nutrients. Finally, the addition of nutrients might adversely affect the hydraulic conductivity of the aquifer through precipitation.

During the design of bioremediation, one must determine the required permits that must be obtained to operate the system.

Monitoring

Design information needed for monitoring includes that related primarily to regulatory compliance and system operation. During the design phase, one needs to determine what information will be required by local, state, and/or federal regulations to determine if remediation is being achieved.

In addition, it is essential that information be obtained to determine if the system is operating effectively. For bioremediation, information such as background carbon dioxide levels and carbon dioxide evolution during operation can be used to determine if the system is operating properly. Another parameter that might be useful is the microbial population levels.

Treatment of By-Products

If by-products, either off-gases or soluble metabolites, are to be produced, information relevant to their treatment must be obtained prior to implementation. Off-gases can be treated via carbon adsorption, catalytic oxidation, or vapor-phase bioreactors. Soluble metabolites often can be treated in the same manner.

Closure

Information relevant to closure includes the closure levels that will be required, final disposition of soils or treated water, risk assessment requirements, disposition of equipment, and post-closure monitoring requirements.

Bioremediation can be a very effective method for treating soils and ground water contaminated with organic wastes. It has many advantages over traditional treatment technologies including lower costs, complete destruction of the contaminant, and shorter time to remediate. It is a very site-specific technology, however, and requires a myriad of information to be successful.

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Scale-Up and Design Issues and Cleanup Objectives A Total Quality Management Approach

Ronald J. Hicks
Groundwater Technology, Inc.
Concord, CA

Essence of Total Quality Management

"Doing the Right Thingthe Right Way"

What
Is
Done
Wrong Things
Right
Wrong Things
Right
Wrong Things
Right
Right
Wrong Things
Right
Right

Doing the Right Thing

Key Issues

- Problem Understanding
- Goal(s) Definition
- Technology Selection

Doing the Right Thing

Understand the Problem

- Site
- Contaminant
- Public Health and Safety
- Regulatory Issues

Public Health and Safety Issues

Will Bioremediation:

- 1. Remove or reduce risk associated with contaminant?
- 2. Do so in a timely fashion and at a reasonable cost?
- 3. Present any additional hazards?
 - **■** By-products
 - **■** Bio-hazards

Regulatory Issues

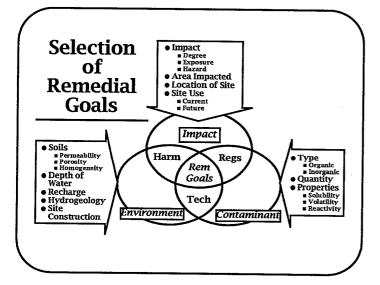
What are the regulations pertaining to:

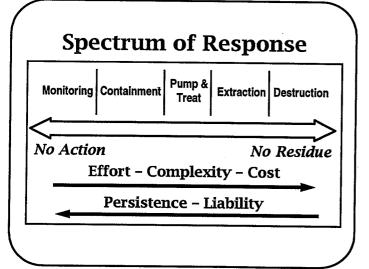
- 1. The contaminant?
- 2. The treatment process?

Doing the Right Thing

Define Goals

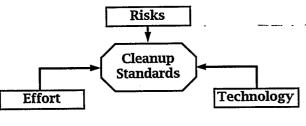
- Cleanup objectives
- Cost objectives
- Time objectives





Doing the Right Thing

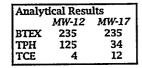
Determining Cleanup Standards

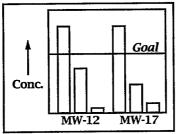


Closure Strategies

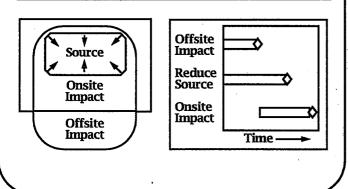
- •Closure as a Point
- •Closure as a Process
- •Closure as a Limit

Closure as a Point

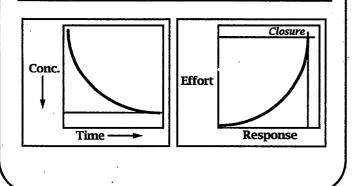




Closure as a Process



Closure as a Limit



 $Hazard \neq Risk$

Risk = f (hazard, exposure)

Risk-Driven Remediation

- Ensures cleanup to acceptable levels based on health and environmental criteria, without excessive costs
- Provides site-specific recommendations

Doing the Right Thing

Technology Selection
In Situ
Bioventing Bioreactors
Slurry Reactors Composting
Bioreactors Aboveground Biocells
Land Treatment

Remedial Effectiveness

Mass Removal Rate (lb/unit time)

Selecting a Bioremediation Technology

Technology Selection Based on:

- 1. Mobility of contaminant or contaminated matrix
- 2. Reactivity
 - **■** Biological
 - Chemical
 - **■** Photochemical

Technology Selection in Bioremediation

	Contaminant Mobility			
	High	Low		
High Reactivity	●Land Treatment ●Aboveground Treatment Cells ●Bioreactors ●In Situ	●In Situ Bioremediation ●Bioventing		
Low	●Bioreactors w/Adapted Population ●Slurry Reactors	●Fungal Treatment ●Biological Stabilization ●Chemical/Biological Treatment		

Doing the Right Thing Design and Implementation

Design parameters are technologyspecific, but are related primarily to:

- Control of contaminant
- Mass transport of amendments
- Monitoring performance and success
- Treatment of by-products
- Closure

Informational Needs for Control of Contaminant (and Amendments)

- Position and thickness of aquifer
- Extent of contamination
- Transmissivity and storage capacity of aquifer
- Hydraulic conductivity and gradient

Informational Needs for Control of Contaminant (and Amendments) (cont.)

- Aquifer boundaries with pumping
- Climate information
- Soil texture and structure
- Topography

Informational Needs for Mass Transport

- Mass of contaminant
- Air permeability
- Adsorptive capacity
- Hydraulic conductivity
- Reactivity of aquifer sediments to amendments

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TO THE SECRET LEADING THE SECRET SERVICE

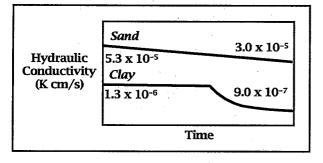
Feasibility Study

- Nutrients
 - 10, 50, 100 ppm nutrient solution tested
 - 10 ppm optimum with 62 percent petroleum hydrocarbon removal in 11 days
- Soils
 - Samples from 8-ft, 13-ft, and 18-ft zones
 - Lithology: Silt Sand → Coarse Sand → Gravel

Feasibility Study (cont.)

Soil Sample Depth	H ₂ O ₂ Reactivity	Hydraulic Conductivity Reduction	Nutries PO ₄	nt Adsorption NH ₄
8 feet	90%	80%	56%	No change
13 feet	49%	No change	86%	15%
18 feet	78%	No change	74%	53%

Effect of Nutrient Addition on Hydraulic Conductivity



Walter Street Committee Co

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Informational Needs for Monitoring **Performance and Success**

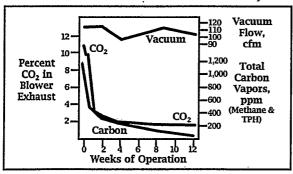
- Mass balance of contaminant
- Rate and extent data
- By-products expected (e.g., CO₂ production)
- Closure levels
- Microbial population/Ecology

Remediation Results

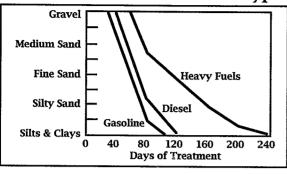
Process	Mass Removed
Phase separated product recovery Volatilization Biodegradation ^A Total	1,510 lbs 780 lbs 33,300 lbs 35,590 lbs
Total ground water recovered and reinjected	8,835,598 gal (≥15 pore volumes)
Initial Contaminant Mass Estimate	25,800 lbs

chanted from CO, measurements from the vapor extraction system efficient. CO, me er converted into contaminant mass removal rates using the following conservative 1. Twenty percent of the extrion dioxide was produced from the biodegradation of 1. Twenty organic matter, 2. Forty percent of the biodegraded organic carbon was evolved as carbon dioxide.

Correlation between Carbon Available and CO₂ Produced with Vented Bioremediation System



Rates of Biodegradation as a Function of Product and Soil Type

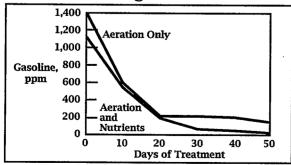


Achieving Target Levels and Predicting Cleanup Times

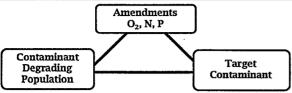
Dependent on:

- Maximum rate and extent as determined by treatability study
- Rate at which amendments can be added
- Ability to optimize system

Effect of Nutrient Addition on Biodegradation



Achieving Target Levels and Predicting Cleanup Times



Success of bioremediation is dependent upon bringing together the organisms, amendments, and the contaminant in both space and time

Predicting Cleanup Times

- Treatability Data Not Always Predictive
 - Container effects (reactor design)
 - Nonrepresentative site samples
 - **■** Highly optimized conditions

Predicting Cleanup Times

- Environmental Factors
 - **■** Temperature
 - **■** Precipitation

Kinetic Illustration

Assumption: Non-Steady-State System

Reaction Rate=ds/dt

 $ds/dt=KS_t$ (equation 1)

K=Reaction constant

S = Reaction/substrate

t = Time

Modification of Equation for Temperature Effect

 $ds/dt=A=K \bullet \chi \bullet f(S_t)$ (equation 2)

A = Biological activity= $f(T^o, S_t)$

 $\chi = Biomass$

 $K = f(T^o)$

Predicting Cleanup Times

- Statistically Valid Experimental Design
 - Mean, standard deviation, coefficient of variation
 - Significant differences of means for treatment effects
 - » Student's T-Test
 - » Analysis of variance
 - » Correlation and regression analysis
 - » Analysis of co-variance

Predicting Cleanup Times

- Mathematical Models
 - Lack of effort in development
 - **■** Insufficient data
 - **■** Invalid assumptions
 - **■** Critical for scale-up

Predicting Cleanup Times

- Kinetic Rate Constants
 - **■** Half-life
 - **■** Michaelis Menten
 - **■** Reaction order
 - **■** Critical for modeling

Treatment of By-products

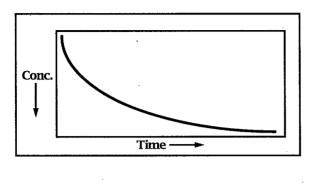
Vapors

- **■** Carbon
- **■** Catalytic oxidation
- Vapor phase bioreactors »Compost »Soil Bioremediation Cells

Soluble

- **■** Carbon adsorption
- **■** Recirculation
- Alteration of metabolic processes (e.g., anaerobic/aerobic)

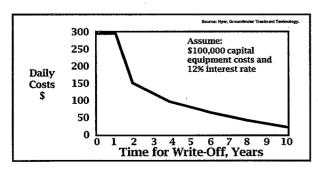
Life Cycle Design



Life Cycle Design

- Time effect on parameters
- Capital costs
- Operator expenses

Capital Equipment Costs

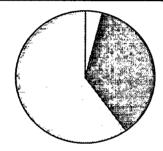


Operational Expenses

Assume:

- \$100,000 capital costs
- 10-year life of equipment
- 12% interest rate
- 15 hp for power (\$0.06/kWh)
- \$3/day chemical cost
- \$10/hour for operator

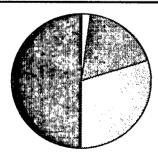
Operational Expenses with No Operator Attention



Chemicals 4%
Power 36%
Equipment 60%

Source: News, Grounderster Treatment Technolog

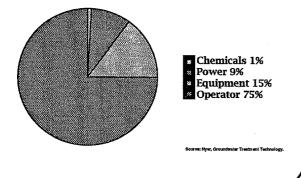
Operational Expenses with 8 Hours/Day Operator Attention



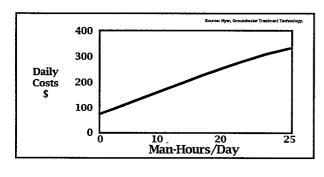
Chemicals 2%
Power 18%
Equipment 30%
Operator 50%

Source: Hyer, Grounderster Treetment Technolog

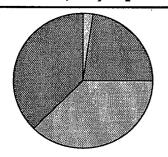
Operational Expenses with 24 Hours/Day Operator Attention



Operational Expenses Summary



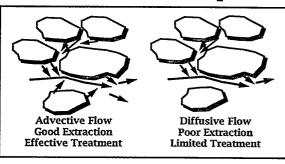
Operational Expenses with \$500,000 Capital Equipment and 24 Hours/Day Operator Attention



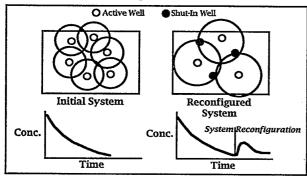
Chemicals 2.3%
Power 22.7%
Equipment 37.5%
Operator 37.5%

Source: Nyer, Groundwater Treetment Technolog

Loss of Remedial Effectiveness at End of Cleanup



Optimizing Performance



Complex Problems Require Integrated Solutions

- No silver bullets
- Complex problems are combinations of simple problems
- Complex solution is integration of simple answers

REACTORS FOR TREATMENT OF SOLID, LIQUID, AND GASEOUS PHASES

Chris Nelson Groundwater Technology, Inc. Englewood, CO

and

Richard Brenner, John Glaser, and Paul McCauley Risk Reduction Engineering Laboaratory U.S. Environmental Protection Agency Cincinnati, OH

Biological treatment is becoming standard technology for treating organic contaminants in the environment. For aboveground treatment of contaminated ground water, bioreactors have the advantage over mass transfer technologies such as air stripping or carbon absorption in that biological action is capable of converting contaminants to innocuous end products such as carbon dioxide and water. Other technologies capable of complete destruction, such as chemical oxidation or incineration, tend to have higher operating costs. A wide range of chemicals can be treated cost effectively by biological treatment in reactors.

Bioreactors utilizing fixed bacterial films are able to overcome many of the potential problems faced in treating contaminated ground water. The biofilm is stable to a wide range of fluctuating contaminant concentrations and mixtures encountered in ground water treatment. The biofilm can withstand sudden high concentrations shocks and remain stable in the presence of very low contaminant loadings. The bacteria attach to support media and provide a stable biomass within the reactor. These reactors can be operated with a minimum of sludge formation. The stability of the film allows long-term operation with minimal operator attention.

Bioreactor technology has been successfully implemented at a number of sites. Treatment efficiency is dependent on correct sizing and evaluation of operational parameters. Removal rates can be greater than 99 percent with proper design. Reactors capable of treating high levels of contaminants also have been integrated with other forms of water treatment to yield highly effective processes. Bioreactors are especially effective for the treatment of soluble contaminants, such as phenol, acetone, or alcohols, which cannot be efficiently removed by air stripping or carbon absorption. Reactors also can provide cost-effective alternatives for the treatment of volatile

contaminants, such as benzene and toluene, when carbon loading is very high or off-gas treatment is necessary.

The biological treatment of soils and sludges represents a significant remedial tool. This technology is widely used to treat soils under a wide range of conditions and for a wide range of contaminants. Contaminants ranging from gasoline to heavy fuels, as well as plasticizers, coal tars, creosotes, and various solvents, have been degraded successfully in soil piles. Soil conditions ranging from sand and gravels to low permeable sludges have been treated successfully.

While the biological treatment of soils and sludges is a versatile tool, it is not without its limitations. As a result, a proper understanding of this technology is necessary for its proper use. This understanding involves both microbiological and engineering aspects. When properly designed and operated, soil biological treatment is a cost-effective technology; when misapplied, it is a costly pretreatment for disposal.

From the microbiological standpoint, it is important to understand the key process variables and the limitations of the technology. The key process variables are those factors that influence the rate and extent of biodegradation. From the engineering standpoint, the focus is on factors that affect the integrity or the performance of the system. The three areas of concern are containment, soil conditioning, and the type of aeration system.

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Reactors for Treatment of Solid, Liquid, and Gaseous Phases

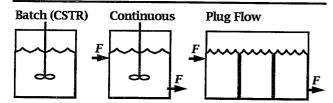
Groundwater Technology, Inc.
Englewood, CO
and
Richard Brenner
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH

Chris Nelson

Bioreactor Presentation Outline

- Bioreactor Theory
- Aqueous Bioreactors
 - Aerobic
 - Anaerobic
- Vapor Bioreactors
- Soil Bioreactors
 - **Biopiles**
 - **Slurry Reactors**

Bioreactor Overview



Fixed Film or Suspended Growth

Goal:

Control Important Environmental Conditions to Maximize Contaminant Degradation

Biological Reactor Approaches

- ullet Conventional
 - **■**Aerobic Metabolism
 - **■**Anaerobic Metabolism

Biological Reactor Approaches (cont.)

- Emerging
 - Sequential Anaerobic/Aerobic
 - Co-Metabolism

 »Methane induced

 »Aromatic induced
 - **Lignin-Degrading Fungi (White Rot Fungi)**
 - **■** Genetically Engineered Microorganisms

Mass Balances

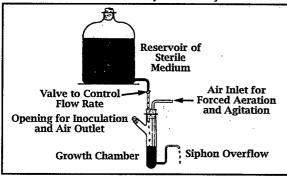
$$F, S_0, X_0 \rightarrow V, X, S \rightarrow F, X, S$$

Accumulation = Inflow - Outflow - Consumption

$$-\frac{ds}{dt} = \frac{\underset{\mathsf{II}}{\downarrow} \mu_{\mathsf{m}} XS}{Y(K_{\mathsf{s}} + S)}$$

Contaminant O₂ + Nutrients \rightarrow CO₂ + H₂O + Inorganic Salt

Laboratory and/or Pilot Studies Should Be Conducted to Accurately Size Any Bioreactor



Important Parameters to Monitor and Control

- Bacterial Concentrations
- Nutrient Concentrations
- Electron Acceptor (e.g., O₂)
 Concentrations and Transfer Efficiency
- pH
- Temperature
- Residence Time

Important Parameters to Monitor and Control (cont.)

- Moisture (Soil and Vapor)
- Contaminant and Other Organic Concentrations (Influent and Effluent)
- Flow Rate (Loading Rate)
- Off-Gas Concentrations (Biological and Contaminant)
- Availability of Contaminant, Bacteria, and Amendments

Important Parameters to Monitor and Control (cont.)

- Influent Pretreatment Requirements
 - **■** pH adjustment
 - **■** Inorganics removal
- Effluent Treatment Requirements
 - Solids removal
 - **■** Carbon polishing

Applicable Media for Bioreactor Treatment

- Water
- Vapor
- Soil

Aqueous Aerobic Bioreactors

Types of Aqueous Bioreactor Designs

- Activated Sludge
- Fluidized Bed
- Sequencing Batch
- Trickling Filter
- Fixed Film

Bioreactors

Selection Criteria

- Contaminant Properties
 - **■** Biodegradability
 - Solubility and Volatility
 - Adsorptivity
- Effluent Requirements
 - Air Discharge Limits
 - **■** Water Discharge Limits

Bioreactors

Fixed Film Bioreactors

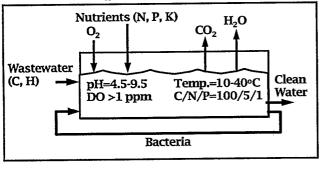
- **Low Organic Loading**
- Retained Biomass
- Minimum Sludge Formation

Bioreactors

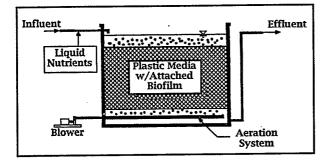
Suspended Growth Bioreactors

- High Organic Loading
- More Complete Mixing

Bioreactor Overview (Suspended Growth)

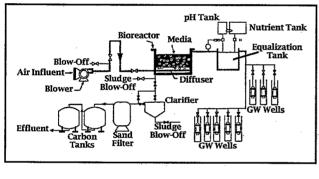


Submerged Fixed-Film Bioreactor Schematic



Biofilm Growth and Detachment A Diffusion of Oxygen and Noutrients to Media Surface through Biofilm Aerobic Layer Plastic Media Anaerobic Layer Plastic Media Increasing Growth B C Biofilm Has Become Too Thick Oxygen Can No Longer Reach the Surface of Media Anaerobic Cause Detachment at Media Increasing Growth Detached Solids Lost to Effluent

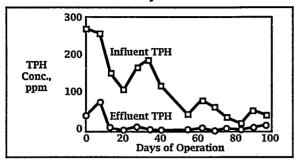
Schematic of Bioreactor System for Ground Water Treatment



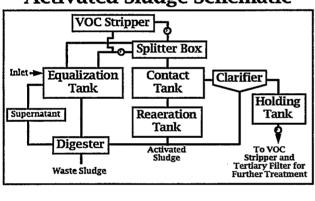
Biological Reactor Results Contaminant-Gasoline

	Influent (ppb)	Effluent (ppb)
Benzene	45.0	<0.5
Toluene	6.9	<0.5
Ethyl B	0.6	<0.5
Xylene	35.0	<0.5
BTEX	88.0	<0.5
TPH	1,300.0	<0.5

Biological Treatment of Petroleum Hydrocarbons



Activated Sludge Schematic



Activated Sludge Bioreactor Performance Data

•	Influent (ppb)	Effluent (ppb)	Removal (%)
Acetone	100	<100	100
Benzene	120	26	78
2-Butanone	<100	<100	NA
Chlorobenzene	180	40	78
Chloroform	<5	<5	NA
2-Chloroethyl Vinyl Ether	<10	<10	NA

Activated Sludge Bioreactor Performance Data (cont.)

	Influent (ppb)	Effluent (ppb)	Removal (%)
1,1-Dichloroethane	750	200	73
1,2-Dichloroethane	100	44	56
1,1-Dichloroethene	70	8	89
trans-1,2-Dichloroethen	e 12	5	58
1,2-Dichloropropane	21	. 7	67
Ethylbenzene	270	16	94
4-Methyl-2-pentanone	300	<50	100
Methylene Chloride	31	<5	100
Tetrachloroethane	25	<5	100

Activated Sludge Bioreactor Performance Data (cont.)

	Influent (ppb)	Effluent (ppb)	Removal (%)
Toluene	1,000	110	89
Trichloroethene	250	49	80
1,1,1-Trichloroethane	120	17	86
1,1,2-Trichloroethane	<5	<5	NA
Vinyl Chloride	160	<10	100
Xylenes (total)	700	37	95

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Aqueous Anaerobic Bioreactors

CONTROL OF SYNTHETIC ORGANIC CHEMICALS
BY THE ANAEROBIC, EXPANDED-BED, GAC BIOREACTOR

WHY GRANULAR ACTIVATED CARBON?

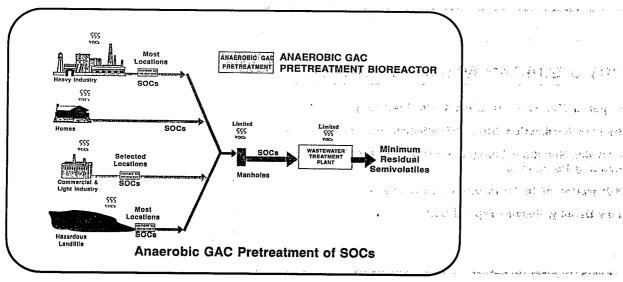
- Superior Microbial Attachment and Sheltering
- Permits Acclimation While Still Meeting Effluent Standards
- Provides Substrate Storage and Resistance to Perturbed Loading Conditions
- Adsorption of Toxic/Hazardous Compounds
- Low Density, Easy-to-Expand Bed

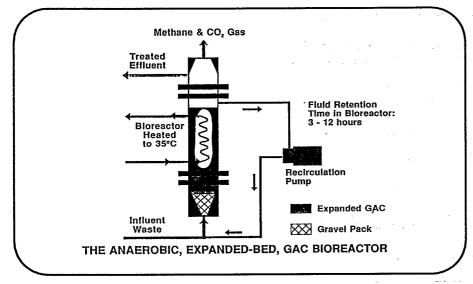
COMPARISON OF ANAEROBIC AND AEROBIC EXPANDED BEDS

- Anaerobic
 - **■** Better Dechlorination
 - **■** Lower Biomass Yield
 - Less Particle Growth and Carry Over
 - Can Handle Higher Organic Concentrations
 - Produces Usable End Product (Methane)
 - Responds Better to Interrupted Operation
- Aerobic
 - Requires Less Operating Controls (pH, temp., etc.)
 - **■** Faster Kinetics/Smaller Reactor
 - **■** Requires Oxygenation
 - Potential Stripping of VOCs

EXPANDED BED VS. PACKED BED ANAEROBIC BIOREACTORS

- Expanded Bed
 - High Specific Surface Area (4,600 m²/m³ for 1-mm dia. particle and 30% bed expansion)
 - Detention Time: 1-12 hr
 - Energy Intensive (for bed expansion)
 - Can Handle Some Solids Loading Without Plugging
 - Requires Skilled Operator
- Packed Bed
 - Low Specific Surface Area (100-200 m²/m³)
 - Detention Time: 12 hr-4 days
 - Net Energy Producer
 - Susceptible to Solids Plugging
 - **■** Easy to Operate





IMPORTANT FEATURES OF THE ANAEROBIC GAC BIOREACTOR

- Combines Adsorption, Biodegradation, and Biogeneration of the GAC Medium
- Aerobically Recalcitrant Chlorinated VOCs are Degraded by Reductive Dechlorination
 e.g., PCE →TCE → DCE → Ethylene
- Low Sludge Production

ANAEROBIC GAC PROCESS LIMITATIONS

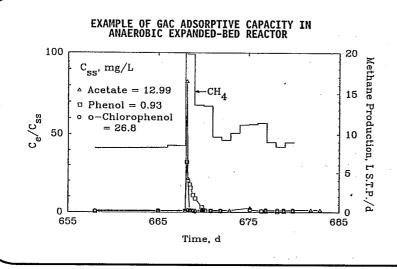
- Desirable bioreactor operating temperature is 35°C
- Not suited for wastes with high suspended solids concentrations
- A few compounds, such as chloroform and carbon tetrachloride, may inhibit reactor performance above 2 mg/L

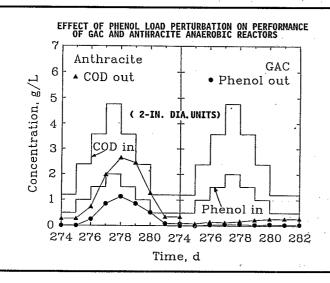
EXAMPLE OF GAC ADSORPTIVE CAPACITY IN ANAEROBIC EXPANDED-BED REACTOR TREATMENT OF o-CHLOROPHENOL

- System Operation
 - Steady State
 - Volumetric Loading Rate = 22 g COD/kg GAC-d
- Steady State Performance

Component	Influent (mg/L)	Effluent (mg/L)
Phenol	1,000	0.93
Acetic Acid	2,000	12.99
o-Chlorophenol	2,000	26.80

- Accidental Slug Loading
 - On Day 668, a slug dose of 8 L of feed containing 8 g Phenol, 16 g Acetic Acid, and 16 g o-Chiorophenol was accidentally introduced into reactor
 - Normal feed was then continued
 - Impact of slug loading on performance shown on next graph





CHLORINATED ALIPHATIC VOCs TREATED BY THE ANAEROBIC GAC PROCESS*

Compound	Influent Conc. (mg/L)	% Removal
Perchloroethylene	20	>99
Trichloroethylene	0.4	>98
Dichloromethane	1.2-20	>96
1,1,1- Trichloroethane	20-400	>99
1,1- Dichloroethane	0.1	>87
Carbon Tetrachloride	20	>99
*4-in, dia. Pilot Units		

AROMATIC AND KETONE VOCs TREATED BY THE ANAEROBIC GAC PROCESS*

Compound	Influent Conc. (mg/L)	% Removal
Chlorobenzene	1.1 - 20	>85
Ethylbenzene	0.6	>86
Toluene	8.2 - 20	>87
Acetone	10 - 755	>96
Methyl Ethyl Ketone	12	>97
Methyl Isobutyl Ketone	10	>94
4-in, dia, Pilot Units		

SELECTED SEMIVOLATILES TREATED BY THE ANAEROBIC GAC PROCESS*

Compound	Influent Conc. (mg/L)	% Removal
Lindane	10	>99
Naphthalene	30	>99
Phenol	3 - 2,959	>97
o-Chlorophenol	2,000	>98
Pentachlorophenol	1,320	>99
Nitrobenzene	0.5 - 100	>98

CASE STUDY 1 - PRETREATMENT OF HAZARDOUS LEACHATES

Location: EPA Test and Evaluation Facility, Cincinnati, OH

· Scale: Two 4-in. dia. Bioreactors

 Waste Streams: Two Hazardous Leachates Spiked with Consortium of 10 VOCs and 4 Semivolatiles

• Empty Bed Contact Time: 6 hr

Operating Temp.: 35°C

• Study Goal: Effective Pretreatment for Subsequent Aerobic Treatment

CASE STUDY 1 - PRETREATMENT GOALS

- Reduce SOC Levels before Subsequent Aerobic Treatment, Minimizing:
 - Air Stripping of VOCs
 - Poor Dechlorination
 - Pass Through of Semivolatiles
- Reduce Leachate Strength:
 - COD
 - BOD

CASE STUDY 1 CHARACTERISTICS OF LEACHATE A

Parameter	Concentration (mg/L)
Total COD	1,261
Soluble COD	1,183
Volatile Acids COD	143
Sulfate	108
Ammonia	305

Summary: Weak strength, little blodegradable organics present, moderate sulfate concentration

CASE STUDY 1 CHARACTERISTICS OF LEACHATE B

Parameter	Concentration (mg/L)
Total COD	3,616
Soluble COD	3,504
Volatile Acids COD	2,464
Sulfate	23
Ammonia	. 311

Summary: Moderate strength, substantial biodegradable organics present, low sulfate concentration

CASE STUDY 1 EFFECT OF LEACHATE STRENGTH ON SOC REMOVAL

Reactor A - Reducing Potential Resulted Primarily from Sulfate Reduction

Reactor B - Reducing Potential Resulted Primarily from Methanogenesis

CASE STUDY 1 - SYNTHETIC ORGANIC CHEMICALS SPIKED INTO LEACHATES A AND B

Volatile Organic Compo	unds (mg/L) * 10,000
Methyl Ethyl Ketone	5,000
Methyl Isobutyl Ketone	1,000
Trichloroethylene	4 0 0
1,1-Dichioroethane	100
Chloroform	5,000
Methylene Chloride	1,200
Chlorobenzene	1,000
Ethylbenzene	600
Toluene	8,000

Semivolatile Organic Compounds (mg/L) *

 Phenol
 2,600

 Nitrobenzene
 500

 Trichlorobenzene
 200

 Dibutyl Phthalate
 200

* Concentrations typical of CERCLA leachates

CASE STUDY 1 - PROJECT OPERATION

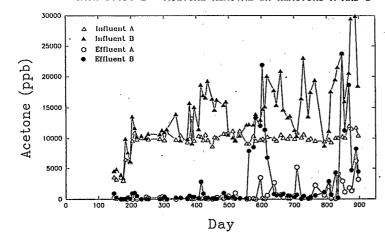
Two Reactors Treating Leachates A and B Containing Spiked SOC Supplement

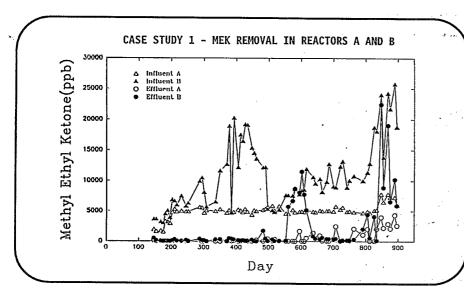
Phases	Days
1. 10 L/day EBCT = 6 hr	0-67
2. 30% SOC Supplement w/o Chloroform	68-105
3. 60% SOC Supplement w/o Chloroform	106-133
4. 100% SOC Supplement w/o Chloroform	134-448
5. Chloroform Addition (2.0 mg/L)	449-553
6. Chloroform Addition (3.5 mg/L)	554-763
7. Chloroform Addition (5.0 mg/L)	764-823

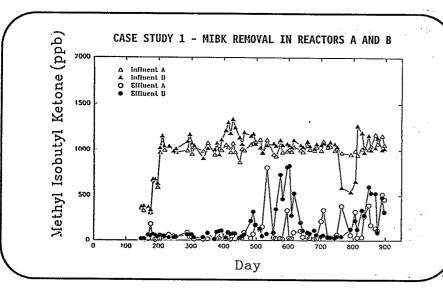
CASE STUDY 1 CHLOROFORM ADDITION

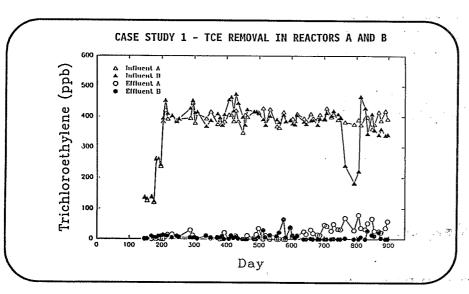
- 2.0 mg/L
 - Reactors A and B Successfully Adapted to the New Feed
- 3.5 mg/L
 - Reactor A Continued to Successfully Treat Leachate A Feed Supplemented with 300 mg/L Sulfate
 - Reactor B Gas Production Ceased within 1 Week (Failure)
- Follow-On Operations
 - Reactor A Continued to Successfully Treat Leachate A Containing 5.0 mg/L Chloroform and 300 mg/L Sulfate
 - Reactor B Recovered after Chloroform Removed from Feed

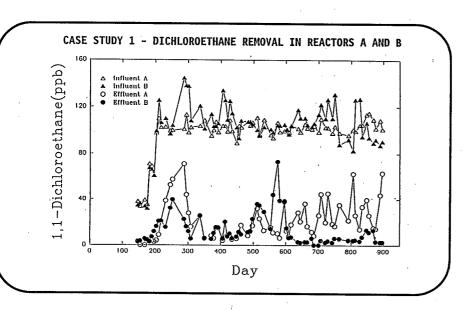
CASE STUDY 1 - ACETONE REMOVAL IN REACTORS A AND B

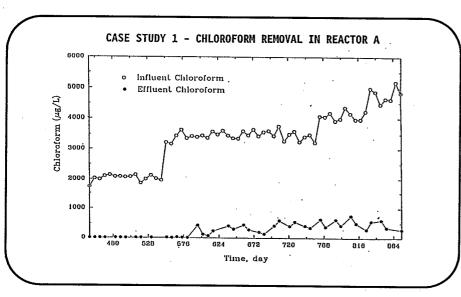


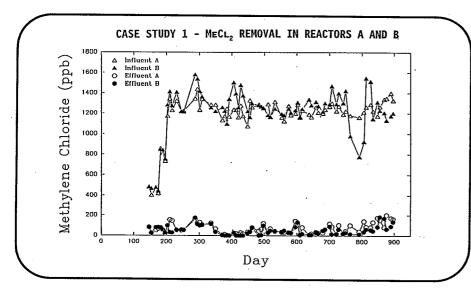


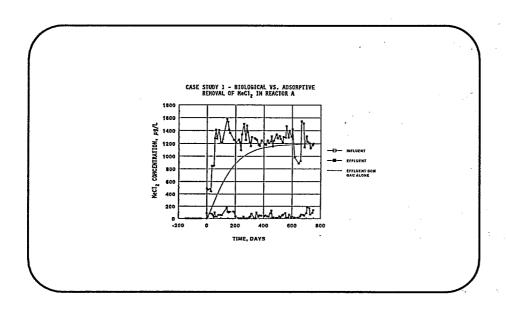


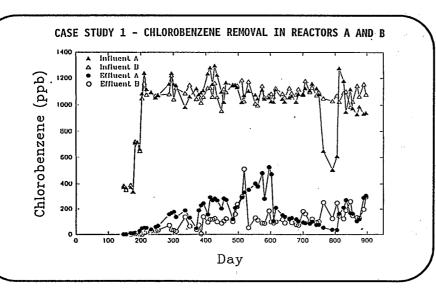


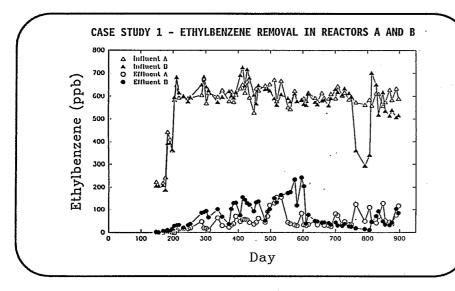


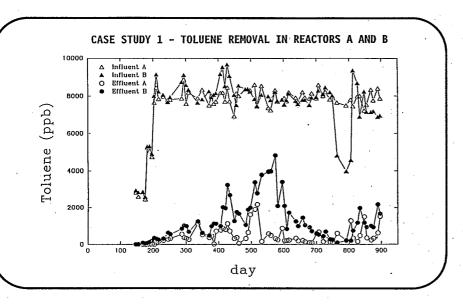


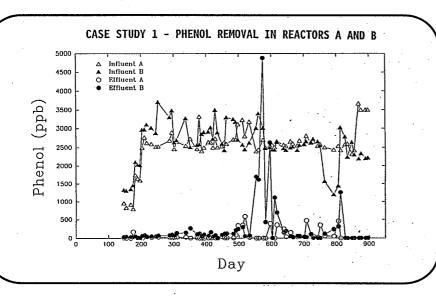


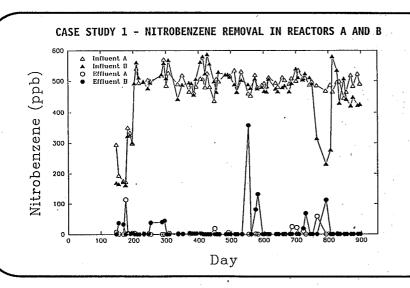


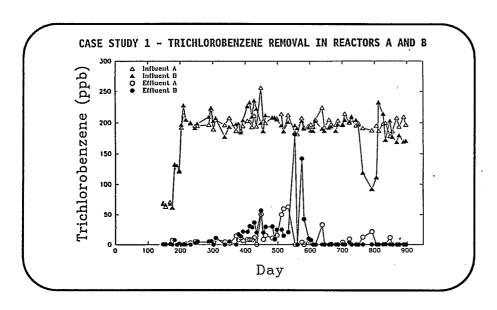


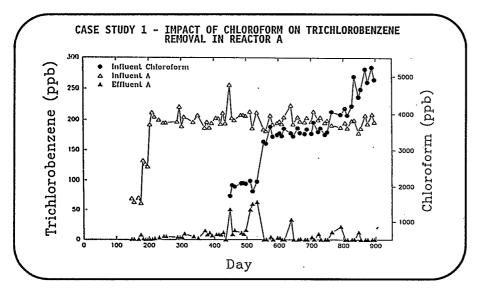


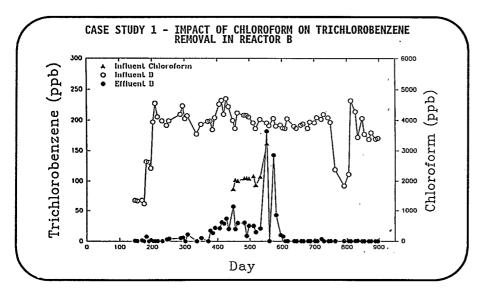


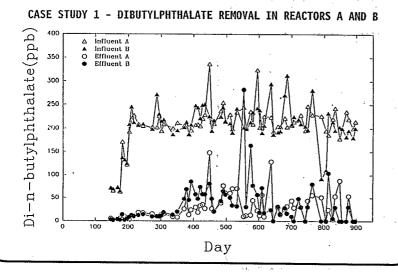












CASE STUDY 2 PRETREATMENT OF PROPELLANT PRODUCTION WASTEWATER

- Site: Radford (MD) Army Ammunition Production Facility
- Major Waste Constituents: DNT, Ethanol, and Ether
- Successful Treatment at Bench Scale on Synthetic Waste at 12-hr Detention Time (4-in, dia., 10-L volume)
 - Complete Disappearance of Ethanol and Ether
 - Complete Transformation of DNT to Diaminotoluene (DAT)
 - DAT Easily Oxidized Aerobically
- Above Unit Transported to Radford and Operated Successfully on Real Production Facility Waste Stream
- Pilot Unit (4-ft dia., 1-gpm flow) is in Design for Scaled-Up Testing and Detention Time Optimization at Radford

REPRESENTATIVE ANAEROBIC GAC BIOREACTOR SIZES

Industrial Pretreatment Flow (gpd)*	Typical Bioreactor Size Range (gal)	
10,000	1,750 - 2,500	
100,000	17,500 - 25,000	
500,000	85.000 - 125.000	

^{*} Assumes influent COD = 2,000-4,000 mg/L

EXISTING ANAEROBIC GAC PROCESS FIELD APPLICATIONS

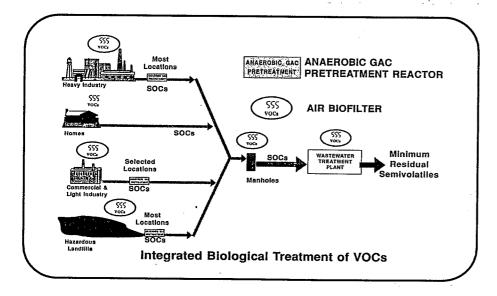
- Envirex Corp., Milwaukee (Mobile Units, Both Anaerobic & Aerobic)
 - Contaminated Ground Water (Primariliy BTEX)
- Liege, Belgium Coke Oven Wastes
- Nizhnii Novgorod, Russia Electronics Plant Solvent Wastes (6-ft dia.)

SUMMARY

- Anaerobic, Expanded-Bed, GAC Bioreactor has been Successfully Tested for Pretreatment of:
 - Hazardous Leachates at Pilot Scale
 - Hazardous Industrial and Commercial Wastes at Pilot and Full Scale
- Process Ready for Broad Range of Field Applications

Vapor Bioreactors

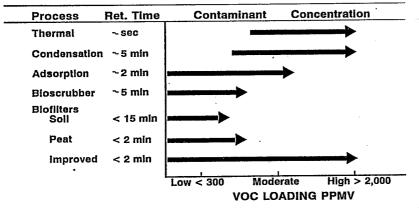
CONTROL OF VOLATILE ORGANIC CHEMICALS BY THE AIR BIOFILTER



VOC AIR EMISSIONS

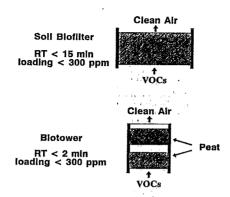
- Increased Health Risk
- Control Applications
 - Direct Industrial and Commercial Releases
 - Superfund and RCRA Sites
 - Contaminated Drinking Water, Ground Water and Wastewater
- Cost-Effective Solution
 - Improved Air Biofilter Technology

VOC CONTROL TECHNOLOGIES



ADVANTAGES OF AIR BIOFILTRATION

- Low Capital and Operating Costs
- Low Energy Usage
- Simple Design and Operation
- Destroys Compounds Unlike Some Other VOC Control Technologies (Condensation, Adsorption)



COMMERCIAL BIOFILTERS

EXISTING COMMERCIAL BIOFILTERS

- ClairTech (Netherlands)
 - Trade Name: "Bioton" System
 - Marketed in USA by Ambient Engineering Co., NJ
 - Media: Peat with Bulking Agents and Solid **Nutrients and Buffers**
 - Installations: Worldwide
- Biofiltration, Inc. (Florida)
 Trade Name: "Bikovent" System
 - Media: Multiple Choices, e.g., Compost, Wood Chips, and Mulch Mixture or Soil with **Appropriate Solid Nutrients and Buffers**
 - Installations: Worldwide
- TNO (Dutch Research Organization)
 - Media: Peat, Compost, and Bulking Agents Mixture
 - Installations: 20 Units Built for Dutch Gas Utility

REPORTED EUROPEAN PERFORMANCE

Hydrogen sulfide	Removals % ~99
Dimethyl sulfide	~91
Turpene	~98
Organo-sulfur gases	~95
Ethyl benzene	~92
Tetrachloroethylene	~86
Chlorobenzene	~69

CASE STUDY - MONSANTO CHEMICAL CO.

- Two Full-Scale Bikovent Compost Biofilter Systems Started Up in Nov. 1992 at Polymer Plants in Springfield, MA, and Trenton, MI
- Installed by Monsanto to Achieve as a Corporate Goal 90% Reduction in SARA Title III Air Emissions between 1987 and End of 1992

DESIGN INFORMATION FOR MONSANTO BIOFILTERS

- Media Area: 7,000 sq ft (approx. 120 ft x 60 ft)
- Media Depth: 4.5-5.0 ft
- Media Composition: Compost, Wood Chips, and Mulch
- Top Layer of Media: 6-9 in. of Bark Chips to Prevent Vegetative Growth

OPERATING CONDITIONS FOR MONSANTO BIOFILTERS

- VOC Concentrations: 200-500 ppmv as Propane in Process Air Waste Stream
- VOC Chemicals:
 - Alcohol (highest conc.)
 - Aldehyde (< 100 ppmv)
 - Ester (< 100 ppmv)
 - Minor Quantities of Compounds Derived from the Above Three
- · Air Stream Flow: 20,000 acfm
- Avg. Actual Empty Bed Residence Time: 2 min Assuming Entire Bed is Active
- Air Stream Temp.: 20-35°C
- Air Stream Moisture: Humidified to 95%+

PERFORMANCE DATA FOR MONSANTO SPRINGFIELD BIOFILTER

- Pilot-Scale Tests: 90-95% Removals at 50-60 sec **Residence Time**
- Full-Scale Tests: (Start-Up Date 11/19/92) - Total System Pressure Drop = 1.5 in. H₂0

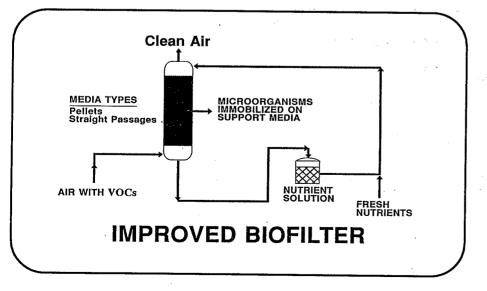
Date of Testing 12/4/92 12/7/92 **Process Exhaust** 260 ppmv 326 ppmv Cooler/Humidier Exhaust 215 ppmv 228 ppmv (Inlet to Biofilter) **Biofilter Exhaust** 15 ppmv 17 ppmv % Removals* **Total System** 95 95 **Biofilter Only** 93

93

*One Minor Compound Not Efficiently Removed (< 90%)

LIMITATIONS OF CURRENT **FULL-SCALE SYSTEMS**

- Not Optimized for Degradation of Important VOCs
- **Applied Primarily to Low VOC Concentrations and Loading Rates**
- Little Data on Performance vs. Contaminants, Loading Rates, and Operating Conditions (e.g., pH)
- Media Becomes Clogged in 1-3 Years and Must be Disposed of



ADDITIONAL ADVANTAGES OF IMPROVED AIR BIOFILTERS

- No Media Replacement
- No Hazardous Media Residue to Dispose of

EPA STUDIES

- Biotower system with pelletized media (activated carbon)
- Tested VOCs Influent Concentration % Removal
 Toluene 520 ppmv >99

 Methylene Chloride 180 ppmv >99

 Trichloroethylene 25 ppmv >99

Nutrients Top View Blofilm Flow Channel Support Plate

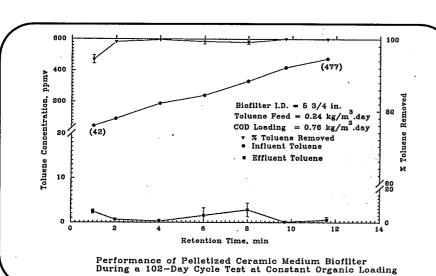
Gas + Contaminants

REMOVAL EFFICIENCIES FOR STRAIGHT PASSAGES BIOFILTER

Chemical	Loading · (ppmv)	Percent Removal
Toluene	450	>99
Methylene Chloride	150	100
Ethylbenzene	20	100
Chlorobenzene	40	>95
Trichloroethylene	25 .	~35

CASE STUDY FOR PELLETIZED CERAMIC MEDIA BIOFILTER

- Location: EPA Test & Evaluation Facility, Cincinnati, OH
- Celite Media
- 5.75-in. Bed Dia.
- 4-ft Media Depth
- Co-Current Gas, Nutrient, and Buffer Flow from Top
- Air Stream Spiked with Toluene



PELLETIZED CERAMIC BIOFILTER (5.75-In. ID) PERFORMANCE BEFORE BACKWASHING (BEGINNING AT DAY 233)

inf. Toluene (ppmv)	Det. Time (min)	Organic* Loading (kg COD/m³/day)	% Toluene Removed	. Head- Loss (in. H ₂ O)	No. of Days of Operation
476	11.8	0.71	100	16	6
505	9.9	0.90	97	19	2
503	7.8	1.13	95	23	7
494	5.9	1.47	99	25	8
503	4.0	2.22	92	42	8

^{*} Typical Loading for Activated Sludge = 1.0 kg COD/m³/day

PELLETIZED CERAMIC BIOFILTER (5.75-In. ID) PERFORMANCE AFTER BACKWASHING* (BEGINNING AT DAY 263)

Day Sampled	inf. Toluene (ppmv)	Det. Time (min)	Organic Loading (kg COD/m³/day)	% Toluene Removed	Head- Loss (in. H₂O)
263	502	4.0	2.21	90	0
266	504	4.0	2.22	89	0.1
267	502	4.0	2.21	89	0.1
268	509	4.0	2.25	89	0,1

^{*} Backwashed with Five Bed Volumes of Water at 10 gpm/sq ft on Day 263

Soil Bioreactors

- ullet Biopiles
- •Slurry Reactors

Aboveground Bioremediation

Treatments Cells (Biopiles)

Treatability of Various Contaminants Availability High (Soluble) Low (Strongly Sorbed) High Treatability Gasoline Diesel Jet Fuel Petroleum Solvents Moderate Treatability Moderate Treatability PAHS API Separator Studge No. 6 Fuel Crude Oil PCBs <1242 Lo-Cl Pesticides Phthalates High BTEX Naphtha Mineral Spirits Phenols Degradability

Low

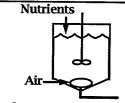
Low Treatability
Chlorinated Solvents
Fuel Additives
MTBE
TBA
Ethers

Very Low Treatability

● PCBs > 1242

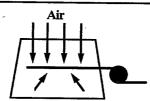
● Hi-Cl Pesticides

Methods of Soil Biotreatment



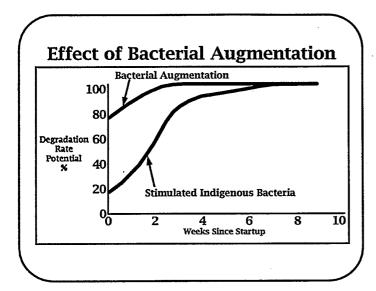
Slurry Reactors

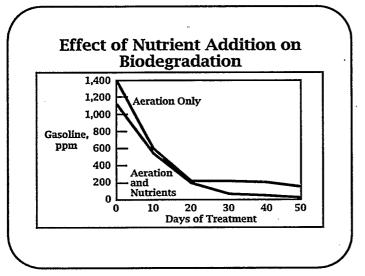
- Aeration by Air Diffusion & **High Turbulence Agitation**
- Nutrients Added as **Solution to Maintain** Threshold Level

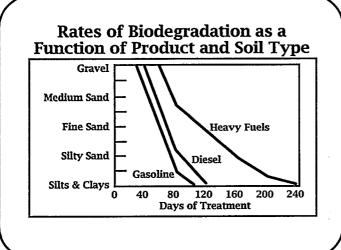


Soil Piles

- Aeration by Mechanical Air Drive (Vacuum or Pressure)
- Nutrients Applied as a Concentrate to Soil Matrix during Construction







Modified Land Treatment Design

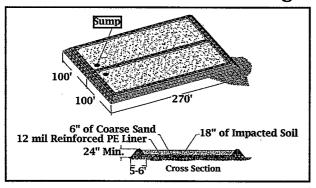
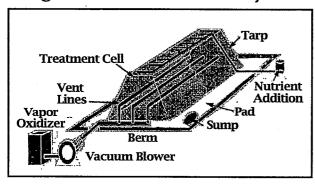


Diagram of Soil Treatment System



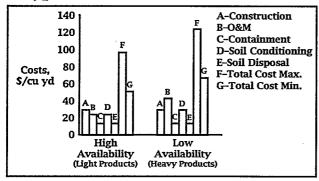
Comparison of Land Treatment & Soil Piles

Parameter/Function	Land Treatment	Soil Piles
Containment	Clean Soil Bed	Pad & Liner
Land Required	36 sq ft/cu yd	3-4 sq ft/cu yd
Oxygenation	Tilling	Mechanical (Vacuum)
Vapor Control	None	Cover/Collection
Nutrient Addition	Spread & Till	Spray & Soak
Soil Conditioning	None (Tilling)	Mechanical/Chemical
Moisture Control	Rain/Till	Spray & Soak
Construction	Soil Spread	Piles & Pipes
Capital	Land & Tractor	Land, Pad, Pumps
Time to Treat	6-12 Months	2-6 Months

Maximum Oxygen Uptake

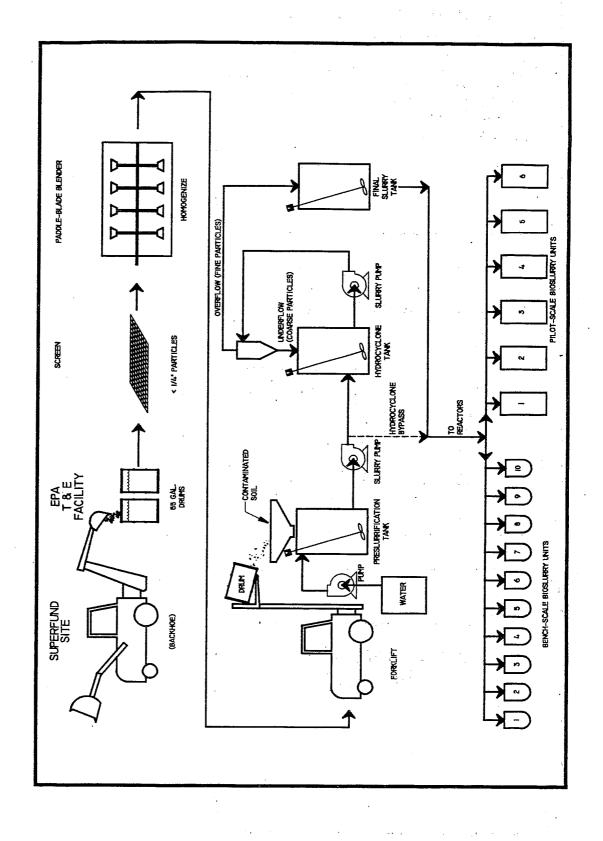
Contaminant Type	Oxygen Uptake (lb O₂/cu yd-day)
Light Hydrocarbons (Gasoline & Jet Fuel)	2.45
Diesel & Fuel Oil	0.33
Sludges	0.026

Typical Costs for Soil Biotreatment

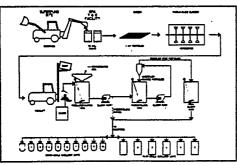


Slurry Bioreactor Technology

SLURRY BIOREACTOR



SLURRY BIOREACTOR TECHNOLOGY



SLURRY BIOREACTOR

 The use of mixing conditions to hasten the biodegradation of soil bound contamination as a suspended water-slurry of the contaminated soil and biomass capable of degrading the targeted constituents of the waste.

SLURRY PHASE BIOREACTORS

- Process description
- Advantages/Limitations
- Targeted waste streams
- Reactor design
- Performance
- Principles

ADVANTAGES/LIMITATIONS

- Advantages
 - more rapid treatment rates
 - greater degree of process flexibility
 - waste containment
 - reduced space limitations
- Limitations
 - higher cost of operation
 - lack of application database
 - optimal operation conditions require investigation
 - normally operated as batch mode
 - few full scale operations, many pliot applications

WASTE STREAMS

- Wood Treating Waste
- Oil Separator Sludge
- · Munitions (soils, sediments, sludges)
- Pesticides
- Halogenated Aromatic Hydrocarbons

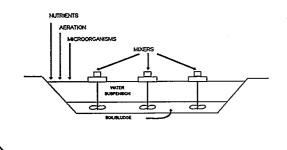
REACTOR CONFIGURATIONS

- Batch
- Sequenced
- · Continuous or semicontinuous

REACTOR DESIGN

- · Aerated lagoons
- · Low-sheer airlift reactors
- Fluidized bed soil reactors (research level)

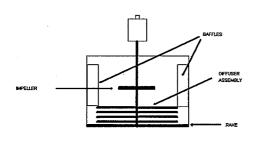
AERATED LAGOON DESIGN



Surface Aeration

- Limited suspension capabilities
- Most applications have poorly determined hydrodynamics
 Control of dead space or holdup locations in the suspension basin
- Poor definition of process controls and process modifications to improve performance

AIRLIFT SLURRY BIOREACTOR



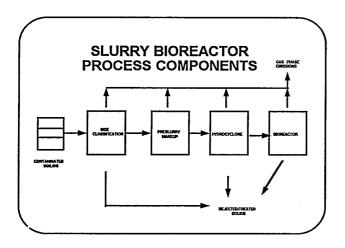
AIRLIFT BIOREACTOR

- · Hydrodynamics more easily understood
- Claims to support treatment of 30-50% solids by weight
- Higher degree of control for:

 - aeration mixing temperature
 - emission control

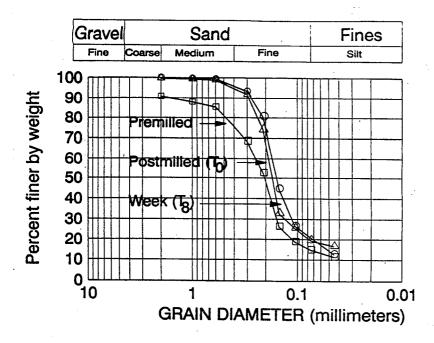
MATERIAL HANDLING

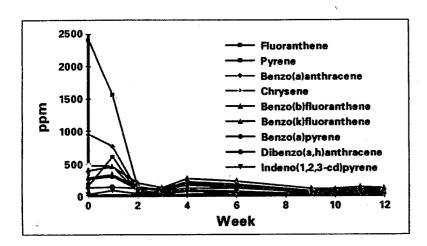
- Size classification equipment
- · Slurry making and pumping capability
- Hydrocyclone for sand fraction rejection for certain reactor configurations
- · Slurry dewatering capability



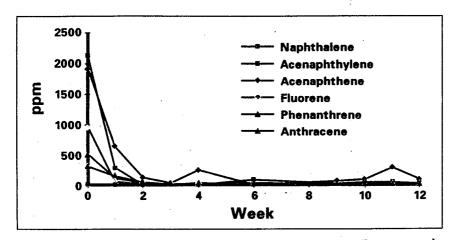
Baseline Soil PA PAH 2- & 3-ring	H Concentrations MEAN (5)	Std. Dev.
	MEAN (5)	Std Day
	mg/kg	mg/kg
Napthalene	2143.3	710
Acensphthylene	17.4	7.6
Acenaphene	1937.1	1016.8
Fluorane	967,8	288,4
Phenanthrène	519.9	12.1
Anthracene	307.0	34.7
TOTAL	5891.5	
		34.7

	EPA BDA		
	Baseline Soil PAH	Concentration	ıs
	PAH 4 E GAY	MEAN (5) mg/kg	Std. Der. mg/kg
_	Fluorezhene	3435.7	732.6
	Pyrecu	161.1	51.2
	Berta(a)erthracere	957.2	264.8
	Chysane	469.1	129.6
	Berg of Difference in the second	399 4	112.7
	Berzefr (Australiana	279 &	83.1
	Berze(e)pyrene	260.2	75A
	Othersto(e,hjurstransera	119.9	94.1
	Indina(1,2,3 cdpyrana	17.2	4.8
	ROTAL.	5001.A	
	TOTALPAH	10972.9	





4- to 6-RING PAHS (SOLIDS, AVG. OF 5 REACTORS)



2- AND 3-RING PAHS (SOLIDS, AVG. OF 5 REACTORS)

SLURRY APPLICATIONS

WOOD TREATING WASTE

SITE	CONTAMBUNTS	RESULTS
Arlewood Inc	PCP, PAHs	PCP & PAH
Omehs, AR		Conc.reduced
		85 and 80%
		56 days
Sadey Creasing, Inc.	Phenol 3.91 ppm	PCP<13.1 ppm
Badey GA	TCP 11.07 ppm	PAHs 0.5,0.03 ppm
	PCP 420 ppm	

SLURRY APPLICATIONS

WOOD TREATING WASTE

STE.	CONTAMBUNTS	RESULTS
IH. Bader	PCP	Mixed Results
RUPERFUNG SITE		
KALINGTON HORTHERN	PAH	4-2.5-ring
MANCRO, MI		PAHs >93%
		12 weeks
COLEMNIEWAS	PCP 400-3,500ppm	PCP degraded
ME,FL		
HCOLLE AND GROS	PCP 2 D00	90% PCP
ME	-3,000 ppm	removal
CW BRIGHTON, MH		

SLURRY APPLICATIONS

WOOD TREATING WASTE

SITE	CONTAMINANTS	RESULTS
SOUTH CAVALCADE ST	PAHs	Lowerrings
HOUSTON, TX		removed in
		preference to
		higher rings

LIMITING FACTOR ANALYSIS

LIMITING	POTENTIAL	CONTROL
FACTOR	MAPACT	STRATEGIES
Waste Composition	inconsistent Trealment	Waste Homogenization
- particle size	Poliutant Release	
Biodegradability	Slower Treatment Rates	Amendments
-solubility		
-surfactants		

LIMITING FACTOR ANALYSIS

LIMITING FACTOR	POTENTIAL IMPACT	CONTROL STRATEGIES
Mixing	Extended treatment periods	Various
-Rheological behavior		
-Particle size		
-Density		
-Aggregate forming		
properties		
Gas Feed	Low treatment	Various
-Density reduction		
 Oxygen uptake 		

LIMITING FACTOR ANALYSIS

LIMITING FACTOR	POTENTIAL IMPACT	CONTROL STRATEGIES
Microbial Population	Rate of Treatment	Amendments
-Nutrients	Title of Titlestone	4
-Oxygen		•
-pH		
-Temperature		
Inhibitory Materials	Toxicity Effects	Removal or Dilution
-Heavy Metals		
-Highly Chlorinated		
Organics		

CURRENT FEED CHARACTERISTICS

- Organics: 0.25- 25% by weightSolids: 10-40% by weight
- . Solids particle size: less than 0.25 inch.
- Temperature: 15-35°C
- pH 4.5-8.8

LIMITING FACTORS Biological

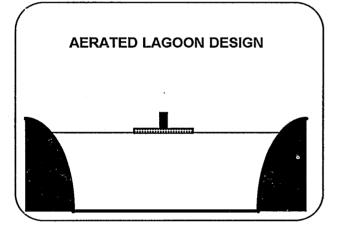
- Microbial population
- Biodegradability of pollutant(s)
- Availability of required nutrient concentrations to growing biomass
- · Oxygen concentration
- pH range

LIMITING FACTORS Physical

- Variable waste composition
- · Wide particle size distribution
- · Inadequate mixing
- Temperature range

LIMITING FACTORS Chemical

- Pollutant water solubility
- Heavy metals
- Highly chlorinated organics
- Some pesticides and herbicides
- · Inorganic salts



ANALYSIS OF PHYSICAL FACTORS

LIMITING	POTENTIAL	CONTROL
FACTORS	IMPACT	ACTIONS
WASTE COMPOSITION PARTICLE SIZE MIXING TEMPERATURE	INCONSISTENT TREATMENT CONTACT MINIMIZATION	

TREATMENT COMPONENTS

- Solid (soil, sludge, sediment)Liquid (water)
- Gas (air, oxygen)

FLUIDIZED SUSPENSION

FLUIDIZED SOIL BIOREACTOR

SOIL TREATMENT: LAND TREATMENT

Daniel F. Pope
Dynamac Corporation
Robert S. Kerr Environmental Research Laboratory
Ada, OK

and

John E. Matthews
Robert S. Kerr Environmental Research Laboratory
U.S. Environmental Protection Agency
Ada, OK

INTRODUCTION

Land treatment involves use of natural biological, chemical, and physical processes in the soil to transform organic contaminants of concern. Biological activity apparently accounts for most of the transformation of organic contaminants in soil, although physical and chemical mechanisms can provide significant loss pathways for some compounds under some conditions.

MICROORGANISMS AND BIOREMEDIATION

Both bacteria and fungi have been shown to be important in bioremediation processes. Most research in bioremediation has centered on bacteria, but fungi can play an important role in bioremediation processes, especially with halogenated compounds. In almost all cases, bioremediation relies on communities of microorganism species, rather than on one or a few species.

Bioremediation consists of using techniques for enhancing development of large populations of microorganisms that can transform the pollutants of interest, and bringing these microorganisms into intimate contact with the pollutants. Several physical constraints on the use of microorganisms for soil remediation are related generally to the problem of bringing contaminants and microorganisms together in close contact under environmental conditions desirable for microbial activity. Generally, a contaminant must move through the waste/soil matrix and pass through a microorganism's cell membrane in order for the microorganism to transform the contaminant, although in some cases contaminants can be transformed by extracellular enzymes without entering

into the microorganisms. Waste compounds that have low solubility in water are slow in moving from soil adsorption sites or free-phase droplets into the soil water and from there into the microorganism. Wastes in solid matrices (soil) have less solvent (water) in which to be dissolved for mobility, are more likely to have highly variable concentrations throughout the matrix, are harder to mix thoroughly, and can be adsorbed onto matrix solids. All of these factors tend to limit accessibility of contaminant compounds to the microorganisms.

LAND TREATMENT TECHNOLOGY

Land treatment techniques most often are directed for treatment of contaminated soil, but certain petroleum waste sludges have long been applied to soil for treatment. Ideally, the contaminated soil can be treated in place (in situ). Often, however, the soil must be moved to a location better suited to control of the land treatment process (ex situ). Land treatment in situ is limited by the depth of soil that can be treated effectively. In most soils, oxygen diffusion sufficient for desirable rates of bioremediation extends only a few inches to a foot down into the soil. Ex situ treatment generally involves application of lifts of contaminated soil to a prepared-bed reactor, which is usually lined with clay and/or plastic liners; provided with irrigation, drainage, and soil water monitoring systems; and surrounded with a berm.

Soil can be screened before application to remove any debris greater than 1 in. in diameter, especially if significant amounts of debris or rocks are present. Any large debris that may adsorb the waste compounds (i.e., wood) should be removed if possible. Small rocks and other relatively nonadsorptive wastes can be treated if they do not interfere with tillage operations.

The soil should be near the lower end of the recommended soil moisture percentage range before tilling, since tilling very wet or saturated soil tends to destroy the soil structure and reduce microbial activity. Tillers tend to mix the soil only along the tractor's line of travel, so tillage should be carried out in varying directions, i.e., lengthwise of the land treatment unit (LTU), crosswise, and on the diagonal.

Once desired target levels of compounds of interest are established, data obtained from the LTU monitoring activities can be statistically analyzed to determine if and when desired levels are reached and the LTU is ready for another lift of soil to be applied.

NUTRIENTS, CARBON SOURCES, AND OTHER ADDITIVES

Land treatment unit microorganisms require carbon sources and nutrients. The nutrient requirements for biodegradation in the field have not been thoroughly studied, and detailed information is not available to indicate the optimal levels of particular nutrients in field situations, so application rates usually are based on nutrient ratios or concentrations developed for crop plants. Fertilizers will supply the nutrients; wood chips, sawdust, or straw can supply carbon. Various animal manures often are used to supply both carbon sources and nutrients. Organic amendments increase the water holding capacity of the soil, which is often desirable in the poor soils found at many plant sites, but can be a liability where land treatment is conducted in areas of high rainfall and poor drainage. Manure should be applied to each lift at the rate of about 3 to 4 percent by weight of soil. Agricultural fertilizer usually is supplied in pelleted form suitable for easy application over large areas of soil. The pelleted fertilizers can be applied with a hand- or tractor-operated cyclone spreader. Soluble fertilizers that can be applied through irrigation systems are available.

Sometimes inorganic micronutrients, microbial carbon sources, or complex growth factors might be needed to enhance microbial activity. Animal manures generally will supply these factors. Proprietary mixtures of various of these ingredients sometimes are offered for sale to enhance microbial activity. Proof of the efficacy/cost effectiveness of these mixtures is lacking in most cases.

The same could be said for microorganism cultures sold for addition to bioremediation units. Two factors limit use of added microbial cultures in LTUs: (1) nonindigenous microorganisms rarely compete well enough with indigenous populations to develop and sustain useful population levels, and (2) most soils with long-term exposure to biodegradable wastes have indigenous microorganisms that are effective degraders given proper management of the LTU.

SOIL MOISTURE CONTROL

Soil moisture should be maintained in the range of 40 to 70 percent of field capacity, allowing soil microorganisms to obtain air and water, both of which are necessary for useful rates of aerobic biodegradation. If soils are allowed to dry excessively, microbial activity can be seriously inhibited or stopped. Continuous maintenance of soil moisture at adequate levels is of utmost importance.

Moisture can be enhanced by traveling gun or similar irrigation systems, which can be removed to allow easy application of lifts. Hand moved sprinkler irrigation systems more often are used, although they usually are more expensive. It is possible to use permanently installed sprinkler systems with buried laterals and mains, but the sprinkler uprights must be avoided when placing lifts and performing other LTU operations. Since one sprinkler will not apply water uniformly over an area, sprinkler patterns should overlap to provide more uniform coverage. The usual overlap is around 50 percent; that is, the area covered by one sprinkler reaches to the next sprinkler. Highly uniform coverage is difficult to achieve in the field, especially in areas where winds of more than 5 mph are common.

The irrigation system should be sized to allow application of at least 1 in. of water in 10 to 12 hours. The rate of water application should never be more than the soil can absorb with very little or no runoff. Since LTUs consist of bare soil, runoff can cause significant erosion very rapidly. Very seldom will application rates of more than 0.5 in. of water per hour be advisable; heavy soils with slopes greater than 0.2 to 0.3 percent will require considerably lower rates of water application. A water meter to measure the volume of water applied is helpful in controlling application.

Surface drainage of the LTU can be critical in high rainfall areas. Soil saturated more than an hour or two greatly reduces microbial action. The LTU surface should be sloped 0.5 to 1.0 percent. Greater slopes will allow large amounts of soil to be washed into the drainage system during heavy rains. Even a slope of 0.5 to 1.0 percent will allow much soil to be eroded; therefore, the drainage system should be designed to allow collection and return of eroded soil to the treatment unit.

Underdrainage generally is provided by a sand layer or a geotextile/drainage net layer under the LTU. The system should be designed so that any water in soil lifts over field capacity will be drained quickly away so microbial activity will not be inhibited. The lifts of contaminated soil usually are placed on a bed of sand or other porous soil. This gives a "perched" water table—the contaminated soil lift will take up water from irrigation or rain until field capacity is reached, then the lift begins to drain excess water into the treatment unit drainage system. The interface between

the lift and the coarse layer underneath should be composed of well-graded materials so that the transition from the (usually) relatively fine soil texture of the lift to the coarse texture of the drainage layer is gradual rather than sudden.

Biological reactors commonly are used to treat leachate prior to discharge. Alternatively, effluent from the biological treatment unit can be applied to the LTU through the irrigation system. Nutrients and microorganisms from the biological treatment system can enhance the microbial activity within the LTU.

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SOIL TREATMENT: DEVELOPMENT AND EVALUATION OF COMPOSTING TECHNIQUES FOR TREATMENT OF SOILS CONTAMINATED WITH HAZARDOUS WASTE

John A. Glaser and Carl L. Potter Risk Reduction Engineering Laboratory U.S. Environmental Protection Agency Cincinnati, OH

INTRODUCTION

Composting is a method of waste treatment whereby the organic component of a solid waste stream is biologically decomposed under controlled conditions to a state in which it can be handled, stored, and/or applied to the land without adversely affecting the environment (Golueke, 1977).

Composting involves a process of biological decomposition of organic components within a complex pile of organic material. Composting seldom occurs naturally since organic waste material in nature is usually distributed in a thin layer over the Earth's surface.

Composting, as a solid waste management tool, is a treatment process involving adding organic material (nutrients and bulking agents) to the solid waste (soil, sludge, sediments) and placing the mixture in a pile. The added organic matter, usually more than 20 percent by weight, provides support to a diverse microbial consortium of aerobic and facultative anaerobic microorganisms. Soil application of composting includes remediation of soil contaminated with munitions, fuels, oily wastes, pesticides, and PAHs.

Composting can be anaerobic, but most methods use aerobic conditions. Bacterial attack on the organic materials is considered to be the "active stage" of composting. The curing stage, a slow process occurring after the active stage, consists of a fungal attack in dryer parts of the pile, and an actinomycete attack in the deeper parts. Optimum conditions for composting may vary depending on a number of factors, but generally 55°C temperature, 40 to 60 percent moisture content, a carbon-to-nitrogen ratio of 20:1 to 30:1, and aerobic conditions with frequent mixing applied to materials with a high surface area are considered best. Bulking agents may consist of sawdust, corn cobs, straw, hay, alfalfa, peanut hulls, rice hulls, or other organic materials.

Mesophilic (35°C to 55°C) composting might prove to be the most effective at destruction of wastes. It might not be practical, however, to maintain a temperature below 55°C from an

economic standpoint if it requires too much energy to keep the temperature that low. Also, thermophilic (> 55°C) conditions might be desirable for pathogen destruction.

Common composting configurations are static pile, windrow, and in-vessel. Windrow composting uses piles arranged in continuous lines called windrows. Windrows are turned frequently for aeration and mixing. Windrow composting is suitable for high volumes of waste, has low capital requirements, offers moderate mixing capability, and has a good oxygen transfer capability. Disadvantages of windrow systems include large space requirements, aeration dependent on operator skill, pile subject to environmental conditions, and limited process control.

Static pile composting uses piles that are not mixed or turned after the composting process has begun. An aeration and heat management system of vacuum or pressure air supply provides some process control. An air exchange manifold of perforated pipe is located under the pile. Air blowers are activated by temperature sensors or gas probes in the pile or piping system. Vacuum systems pull air from the pile surface into the pile, allowing good control of volatile emissions and odors, moisture management by application of water to the pile surface, and even distribution of heating/cooling. The pressure system pushes air into the pile core, allowing gas phase treatment of air stream volatiles from other sources and rapid control of heating/cooling since air moves directly into the pile core.

In-vessel composting, in large closed reactor vessels, typically allows more complete mixing and process control. The system may be highly automated to reduce operator person-hours and facilitate constant data collection. Volatiles are readily controlled since the system is totally enclosed. Reseeding (bioaugmentation) is easily accomplished, and the process is generally faster than other composting methods. On the down-side, in-vessel composting has high capital requirements, and requires more complex equipment, and few data exist concerning the process.

Siting requirements for a compost operation include space for the pile and operations including composting; curing and handling; and storing bulking agents, soil, and equipment. Strategically, siting requires consideration of access, runoff control, proximity to population, and typical public relations problems associated with treatment of hazardous waste.

Composting faces limitations and disadvantages with respect to process control, emissions control, and the extent of remediation. Emissions control requires control of volatiles, odor, leachate, and runoff. Emissions control is especially difficult with windrow systems. Metals and some pesticides can inhibit microbial activity, and some organic compounds might not be metabolized.

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Land Treatment

Daniel F. Pope
Dynamac Corporation
R.S. Kerr Environmental Research Laboratory
and
John E. Matthews
R.S. Kerr Environmental Research Laboratory
U. S. Environmental Protection Agency
Ada, OK

Land Treatment

Biological, chemical, physical processes transform contaminants

Biological Activity

- Most transformation of organic contaminants
- Physical, chemical mechanisms also involved

Ultraviolet Light

- Soil surface
- Higher PAHs

Volatilization

Low Molecular Weight Compounds

- BTEX
- Naphthalene
- Methyl naphthalenes

Hydrolysis

Pesticides

- Amides
- Triazines
- Carbamates
- Thiocarbamates
- Nitriles
- Esters
- Phenylureas

Know Thy Waste

Relative importance of processes varies widely for different compounds under different circumstances

Compounds Amenable To Land Treatment - PAHs

- 2 ring PAHs readily degraded, volatile, leachable
- 3 ring PAHs degradable, leachable
- 4 ring PAHs fairly degradable, leachable
- 5-6 ring PAHs difficult to degrade

Compounds Amenable To Land Treatment

Phenols

- Penta & Tetrachlorophenol
- Difficult over 1000 ppm
- Other phenolics

Compounds Amenable To Land Treatment

Hydrocarbons

- Aliphatics 1-8 C chains
- Readily degradable
- Volatile

Compounds Amenable To Land Treatment

Hydrocarbons

- Most 12-15+ C chains
- Slow degradation
- Relatively immobile
- Relatively nontoxic

Compounds Amenable To Land Treatment

Hydrocarbons

- Branched chain, unsaturated, rings
- Degradable

Compounds Amenable To Land Treatment

BTEX

- Degradable
- Volatile

Compounds Amenable To <u>Land Treatment</u>

- Munitions more often composted
- Phthalates
- Pesticides

Microorganisms and Bioremediation

- Bacteria, fungi important
- Most research on bacteria
- Fungi with halogenated compounds

Microorganisms and Bioremediation

Bioremediation relies on microbial communities

Bioremediation

- Developing large populations of microorganisms that can transform pollutants
- Bringing microorganisms into intimate contact with pollutants

Physical Constraints on Soil Bioremediation

Getting contaminants, microorganisms in close contact under environmental conditions desirable for microbial activity

Constraints

- Contaminant must move through waste/soil matrix
- Pass through cell membrane
- Extracellular enzymes

Constraints

Low Water Solubility (4, 5, 6 ring PAHs)

Slow moving from adsorption sites or free phase into water, then into microorganism

Constraints

Wastes In Solid Matrices (soil)

- Less solvent (water) for mobility
- Highly variable concentrations throughout matrix
- Harder to mix thoroughly
- High tendency to be adsorbed onto matrix solids

Microorganisms

- Most live in water
- Water in tank reactors, aquifers, or thin film of water on a soil particle

<u>Microorganisms</u>

- Sensitive to osmotic potential
- Process waters, contaminated soils high dissolved salts
- Slow changes better

<u>Microorganisms</u>

Electron Acceptor

Most LT Microbes aerobic

Supplying Electron Acceptors

- Injecting air/oxygen supplying compounds
- Tilling soil to allow air to enter

<u>Microorganisms</u>

Water/Oxygen

- Balance between water and oxygen
- More water, less oxygen
- In soil, oxygen/water inversely related

Microorganisms

pН

- pH 6-8
- Pollutant chemistry

Microorganisms

Toxicity

- Heavy metals
- Halogenated organics
- Pesticides

Microorganisms

Toxicity

- Response highly variable
- Treatability study

<u>Microorganisms</u>

- Carbon sources
- Mineral nutrients (nitrogen, phosphorous, etc.)

Carbon, Nutrients

- Pollutants may supply carbon source, some nutrients
- Often nutrients must be supplied

Nutrients

- Agricultural fertilizers
- Manures, etc.

Nutrient Balance

- C:N:P 100-300:10:1
- Carbon degradability

Carbon

Manure, straw, wood chips, sawdust

Cometabolites

- Little research except chlorinated hydrocarbons, anaerobic conditions
- Thought to be necessary for 5-6 ring PAHS
- Possibly supplied in manures, vegetation enhancement

Microorganism Populations

- More microorganisms, faster transformation
- What is being counted?

Microorganism Populations

- Quantitative measure of microorganism population
- Index to microbial environment

Microorganism Populations

- Plate counting
- Respiration
- Total Counts
- Living Counts

Land Treatment Technology

- Contaminated soil
- Sludge application to soil

In-Situ - Ex-Situ

Control - runoff, leachate, volatiles

In-Situ - Soil depth

- Effective oxygen diffusion
- Bioventing for greater depths

In-Situ

- Treat surface soil, remove
- Treat surface soil, deep till

Semi In-Situ

- Remove soil to depth
- Add lifts back to excavation for treatment

Tillage Depth

- Most tractor mounted tilling devices till down to one foot
- Large tractors, specialized equipment till to three feet or more
- Large augers move soil from 50-100 feet to surface, but practicality not fully shown

Ex-Situ

- Application of lifts of contaminated soil to prepared bed reactor
- Clay and/or plastic liners
- Bed of porous soil
- Irrigation, drainage and soil water monitoring systems
- Berm

Land Treatment

Lift Depth

Twelve inches or less preferred

Soil Type

- Limited to 6 to 24 inches of soil
- Limited in heavy clay soils, especially in high rainfall areas
- Oxygen transfer limitations
- Substrate availability

Soil Type

Working With Heavy Soils

- Shallow lifts
- Improve tilth

Improving Tilth

Bulking Agents

Organic Matter

Improving Tilth

High Sodium Content

Add gypsum (calcium sulfate)

Preparing Soil For Application

- Screen to remove debris greater than 1" diameter
- Remove large debris that may adsorb waste compounds

Applying Soil

- Apply lightly contaminated soil at beginning of operation
- Apply manure, nutrients, water until total microorganism populations 106-107 CFU/gram

Tilling

- Enhance oxygen infiltration
- Contaminant mixing with microorganisms

Tilling

- Lower end of soil moisture percentage range before tilling
- Tilling very wet or saturated tends to destroy soil structure, reduce microbial activity
- Wait 24 hours after irrigation or a significant rainfall event

Tilling Schedule

Compromise

Tilling - Mixing

- Mostly along line of travel
- Till in varying directions

Tilling Equipment

- Rotary tiller for tilling, mixing purposes
- Disk harrow not recommended
- Subsoil plow, chisel plow to break up zone of compaction

Tilling

- Subsequent lifts tilled into top 2" or 3" of previous lift
- To mix populations of well acclimated microorganisms

Lift Application Timing

- Based on reduction to defined levels of particular compounds or categories of compounds
- Usually more detailed sampling to determine finish

Nutrients, Carbon Sources, and Other Additives

Carbonaceous ("Organic") Amendments

- Animal manures
- Wood chips, sawdust
- Straw, hay

Carbonaceous <u>Amendments</u>

- Carbon
- Some nutrients
- Bulking agent
- Adsorbent

Carbonaceous Adsorbents

- Slow migration
- May sequester contaminants
- Increase permeability
- Increase oxygen demand
- Increase water holding capacity

Carbonaceous <u>Amendments</u>

Application Rates

- Must be balanced with nutrients
- 3-4% by weight of soil

Carbonaceous <u>Amendments</u>

- Manures often mixed with bedding
- Bulking agent
- Nutrient demand

Carbonaceous <u>Amendments</u>

- Small particle size
- Thoroughly mixed with soil

<u>Fertilizers</u>

- Ammonium nitrate
- Triple superphosphate
- Diammonium phosphate

<u>Fertilizers</u>

- Can cause pH to drop
- Equivalent indicated on bag

<u>Fertilizers</u>

- Pelleted form for easy application
- Unformulated fertilizer difficult to spread evenly
- Hand or tractor operated cyclone spreader

Fertilizers

Soluble Forms

- Can be applied through irrigation systems
- Application rates may be closely controlled
- Applications can easily be made as often as irrigation water is applied
- Immediately available to microorganisms

Fertilizers

Soluble Forms

Equipment meters concentrated nutrient solutions into irrigation system on demand

Soil Nutrient Levels

- Nutrient requirements not thoroughly studied
- Detailed information not available to indicate optimal levels
- Difficult to show response in field

Soil Nutrient Levels

- Soil concentration
- Concentration ratio

Micronutrients

- Carbonaceous amendments
- Inorganic fertilizers

Proprietary Micronutrients

Generally easily supplied with readily available horticultural fertilizers

Complex Nutrients

- Vitamins
- Growth Factors

Complex Nutrients

- Easily shown in lab culture, with defined media
- Difficult to show effectiveness in field

Bioaugmentation

- Indigenous isolated, cultured
- Nonindigenous
- Genetically engineered

Bioaugmentation

Nonindigenous microbes rarely compete well enough to develop, sustain useful population

Bioaugmentation

Most soils with long term exposure to biodegradable wastes have indigenous microorganisms that are effective degraders given proper management of the LTU

Bioaugmentation

Little data from well designed experiments to show efficacy

Soil Moisture Control

40-80% of field capacity

Field Capacity

- Soil micropores filled with water
- Soil macropores filled with air
- Microorganisms get air and water

Soil Moisture

Maintaining 40-80% of FC allows more rapid movement of air into soil, facilitating aerobic metabolism without seriously reducing supply of water to microorganisms

Soil Moisture

- Some evidence that continuous maintenance at high levels better
- Requires careful management

Soil Moisture

- If soils dry excessively, microbial activity seriously inhibited, stopped
- Maintenance at proper level is not trivial

Measuring Soil Moisture

- Gravimetric
- Tensiometer
- Gypsum blocks
- Capacitance effect
- Neutron probe

Irrigation Systems

- Traveling gun
- · Hand moved surface mounted
- Permanently installed buried laterals, mains
- Fire hose

Irrigation Systems

- Operating pressure 30 to 50 lb/in²
- Usual overlap 50%
- Uniform coverage difficult
- Winds > 5 mph problematic

Irrigation Systems

- At least 1" water in 10-12 hours
- No more than 0.5" per hour
- Little or no runoff

Application Rates

- Estimate water uptake rates from Soil Manual data
- Soil Manuals may refer to soils with vegetative cover
- Reduce suggested rates by half

Application Rates

- Water meter to measure volume applied
- Rain gauges at various locations on LTU

Surface Drainage

- Critical in high rainfall areas
- Saturation > hour greatly reduces microbial action

Surface Drainage

- Surface should be sloped 0.5-1.0%
- Greater slopes erosion hazard
- Design to allow collection, return of eroded soil

Internal Drainage

- Sand/gravel layer
- Geotextile/drainage net layer

Internal Drainage

- Lifts usually placed on bed of sand, other porous soil
- Perched water table

Perched Water Table

- Lift takes up water until field capacity
- Then begins to drain excess water
- Lower lift layer may remain overly wet

Internal Drainage

- Interface between lift & drainage layer - well graded materials
- Transition from lift to drainage layer gradual
- Water movement through interface enhanced

Internal Drainage

- Reduces tendency for soil lift to become saturated
- Interface graded by tilling lift into top of drainage layer

LTU Leachate & Runoff

- Recycled onto LTU
- With or w/o treatment
- Treated and discharged

Leachate & Runoff Treatment

- Biological
- Adsorption

Disposal of Treated Soil

- Replace in excavation
- Disposal cell

LT As Part of a Treatment Train

High organics may inhibit solidification /stabilization

LT Disadvantages

- Time
- High Concentrations
- Low Concentrations
- Final Levels
- Space Requirements
- Volatiles/Dust/Leachate

LT Disadvantages

Time

- Slow
- Recalcitrant Compounds Determine Time

LT Disadvantages

High Concentrations

May require mixing with low level contaminants

LT Disadvantages

Low Concentrations

May not cause significant reduction

LT Disadvantages

Final Levels

- Levels below ppm range difficult
- Vegetation enhancement may help

LT Disadvantages

Space

- Treatment area
- Stockpiling area
- Equipment operation

LT Disadvantages

Volatiles

- Maximizing volatiles
- Covers expensive

LT Disadvantages

Dust

Water application

LT Disadvantages

Leachate

- Recycle or treat for ex-situ
- Hard to capture for in-situ
- Reduce mobility
- Control water

LT Costs

- Earthmoving
- Containment
- Monitoring
- Operations
- Volatiles control

Development & Evaluation of Composting Techniques for Treatment of Soils Contaminated with Hazardous Waste

Carl Potter and John Glaser
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH

SOIL COMPOSTING

Definition

... method of solid waste management whereby the organic component of the solid waste stream is biologically decomposed under controlled conditions to a state in which it can be handled, stored, and/or applied to the land without adversely affecting the environment.

Golueke, 1977

COMPOSTING PROCESS

Mix Soil With:

- Bulking Agent (Sawdust, Corn Cobs, Straw)
- Moisture
- Nutrients (Manure, Sludge, Food Scraps)

PRINCIPLES

- Operation can be conducted under both aerobic and anaerobic conditions
- A wide variety of cheap bulking agents are available
- Desired biological activities can be selected by process manipulation
- Can operate under mesophilic and thermophilic conditions
- Inoculation with nonindigenous microorganisms is possible

WASTE STREAMS

- Wood Treating Waste
- Oil Separator Sludge
- Pesticides
- Halogenated Aromatic Hydrocarbons

SOIL COMPOST SYSTEM

Advantages

- Inexpensive
- Very Little Energy Requirement
- Requires Less Soil Screening than Bioslurry

SOIL COMPOST SYSTEM

Disadvantages

- Difficult to Control Volatile Emissions
- Very Slow Process
- Not a Well Controlled Process

LIMITATIONS OF COMPOSTING

- Metals may be toxic to microorganisms
- Metals cannot be eliminated by microorganisms
- Some organic compounds may not be metabolized

CONTROL REQUIREMENTS

- Condensate moisture in the air pulled through the pile
- Leachate drainage from the compost process
- Runoff need to control the amount of precipitation reaching the compost pile

LAYOUT SIZE REQUIREMENTS

- Bulking agent storage
- Mixing
- Composting pad
- Processing (curing)
- Contingency
- Material handling

机多物性 医心内炎 建铁矿 医抗疗

LAYOUT STRATEGIC CONSIDERATIONS

- Access
- Runoff control
- Proximity to population
- Typical public relations problems associated with treatment of hazardous waste

TYPES OF COMPOST OPERATIONS

Static Pile

- Forced air

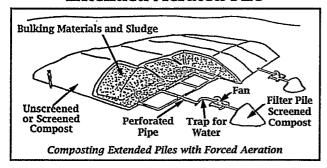
Windrow (Turned Pile)

- Turn pile periodically to aerate

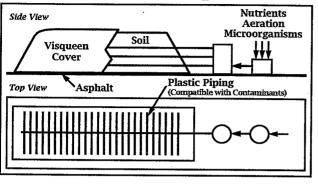
in-Vessel

- Forced air
- Regular mixing
- Climate control

Schematic Diagram of Extended Aerated Pile



Static Pile Composter



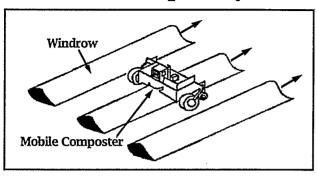
ADVANTAGES Static Pile Systems

- Low capital costs
- More space efficient than windrow
- Process control may be partly automated
- Downflow system can be interfaced with a biofilter to control VOCs

DISADVANTAGES Static Pile Systems

- Requires more land than in-vessel option
- Requires higher energy input than windrow
- Subject to the influence of climate conditions
- Poor control of pollutant fate in treatment system

Windrow Compost System

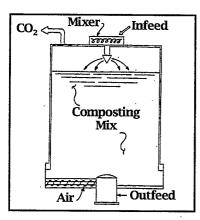


ADVANTAGES Windrow Systems

- Capacity to handle high volume of material
- Relatively low capital investment
 - pad for piles
 - windrow machine
 - front-end loader
- Good oxygen transfer
- Intermediate stage of mixing

DISADVANTAGESWindrow Systems

- Not space efficient
- Equipment maintenance cost can be significant
- Aeration is highly dependent on operator skill
- Subject to changing climate conditions unless covered
- Demands significant moisture control
- Requires large volume of bulking agent
- Poor control of pollutant treatment fate in system



In-Vessel Composter

ADVANTAGES In-Vessel Systems

- Space efficiency
- Improved process control over open systems
- Process control may be automated
- Independent of climate
- Facilitates mass balance monitoring

DISADVANTAGES In-Vessel Systems

- High capital investment
- General lack of operating data
- Process susceptible to mechanical disruption
- Compost compaction may confound results
- Low operational flexibility

GENERAL ECONOMIC CONSIDERATIONS

- Cost of Bulking Agents and Nutrients
- Cost of Excavation

Time Factor (Slow Process)

- Cost of Handling Finished Product
 - Disposal
 - Further Remediation

KEY ECONOMIC FACTORS

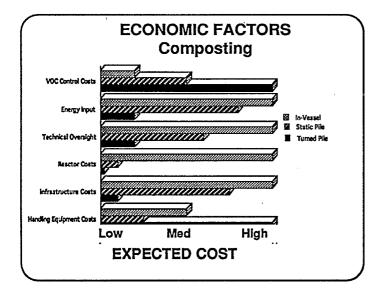
Process Selected

Volume of Contaminated Soil

Soil Throughput

Amendment Costs

Treatment Time



COMPOSTING DEMONSTRATION AT UMATILLA DEPOT

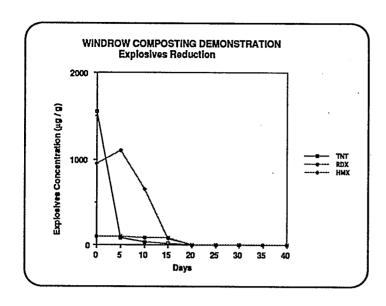
- Windrow Process Design
- Turned Once Per Day
- 55 °C Temperature
- Soil Content 30% (by volume)
- Amendments (by volume)
 - Cow manure
 - Vegetable waste
 - Alfalfa / Sawdust
- 40 Days Treatment Time

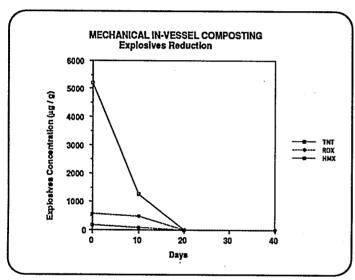
COMPOSTING OF EXPLOSIVES-CONTAMINATED SOILS

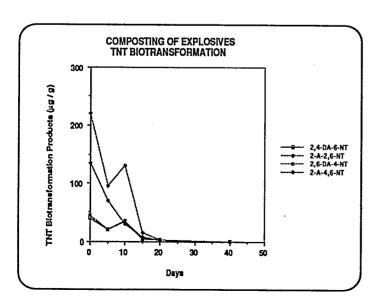
- Applications/Contaminants
 - High Contamination Levels
 - Soils and Sludges
 - TNT, RDX, HMX, Tetryl, DNT, NC
- Advantages
 - Demonstrated Effective
 - Product Is Enriched
 - Various Reactor Configurations
- Disadvantages
 - Minimal Field Experience

WINDROW COMPOSTING EXPLOSIVES REDUCTION

Day	TNT (1-g/g)	RDX (µg/g)	HMX (19/9)	% Reduction TNT RDX HMX		
0	1563	953	156	0.0	0.0	0.0
5	101	1124	158	93.5	0.0	0.0
10	23	623	119	98.5	34.6	23.7
15	19	88	118	8.80	0.7	24.4
20	11	5 .	2	99.3	99.5	98.7
40	4	2	5	99.7	8.00	96.8







COMPOST TOXICOLOGICAL AND CHEMICAL CHARACTERIZATION

- Reduced Toxicity

 → 90 to 98% Reduction in aquatic toxicity
 observed in CCLT leachates
 → No rat oral toxicity detected
 → No mutagenicity observed in CCLT leachates
 → Biotransformation to less toxic compounds
- Chemical binding of radiolabeled TNT to the compost

UMDA FEASIBILITY STUDY Comparison of Alternatives

	INCINERATION	COMPOSTING
Overall Protection	Yes	Yes
Meets Cleanup Requirements	Yes	Yes
Effectiveness	99.99%	97 to 99%
Reduces Toxicity	> 90%	>90%
Long-Term Protection	Yes	Yes
Time	16 Months	24 Months
Effectiveness Reduces Toxicity Long-Term Protection	99.99% > 90% Yes	Yes 97 to 99% >90% Yes

BIOVENTING

Ronald J. Hicks
Groundwater Technology, Inc.
Concord, CA

and

Greg Sayles
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH

Bioventing is an in situ process of moving air through contaminated soils to increase soil oxygen concentrations and stimulate the biodegradation of contaminants by indigenous microbial populations. Bioventing is best suited at a site at which aerobic organisms capable of degrading the contaminant are present and oxygen is limited.

The bioventing process begins by drilling injection wells into the ground where the contaminant exists. The number, location, and depth of the wells depend on the geological, chemical, and microbiological features of the site and other engineering considerations.

Air is delivered to the subsurface by either negative or positive pressure. Some of the advantages and disadvantages of either approach are shown in Table 1.

Each system is designed to bring oxygen into the soil. The oxygen then is used by the indigenous microorganisms to degrade the contaminant. In addition to oxygen, other nutrients might be pumped into the soil either through the wells or through an independent nutrient gallery. By providing the nutritional requirements for microbial growth (i.e., oxygen and nutrients), the microorganisms will use the contaminants in the soil as a food source and convert them to nonhazardous compounds such as carbon dioxide and water.

TABLE 1. Advantages and Disadvantages of Oxygen Delivery System

Oxygen Delivery System	Advantages	Disadvantages
Positive Pressure	No off-gas treatment	Needs extensive soil gas monitoring
	Long gas residence time	Less control of gas flow
	Greater depth of treatment	Limited in shallow environments
Negative Pressure	Control of off-gas	Off-gas treatment likely
	Ease of monitoring process	Limited at deep sites
	Little soil gas monitoring	Off-gas treatment costs

Before considering or designing a bioventing program, appropriate site information needs to be obtained. Site information such as contaminant identity and spatial distribution helps in determining the treatability of the site. Nutrient, pH, moisture content, and cation exchange capacity (CEC) help to determine the mass load and mass transport of required amendments at the site. Performing laboratory treatability studies will help determine the maximum extent of degradation that can be expected and whether cleanup objectives can be reached using bioventing. In addition, air permeability studies, performed either in the laboratory or in field tests, will help determine the design of the oxygen transport system. The identity and mass of off-gases that might be expected can be determined either in laboratory or pilot-scale tests.

The rate of degradation and, hence, the expected time to clean up the site can be estimated during laboratory studies. A more accurate means of determining rates of degradation at the site, however, is to perform an in situ respiration test. This test is performed by aerating the site until the soil gas composition reaches steady state and then monitoring oxygen, carbon dioxide, and contaminant. The results of a respiration test performed at the contaminated site can be compared with background respiration data to obtain oxygen uptake rates. This information can be coupled with mass load data for total utilizable organic compounds (determined in the laboratory) to calculate the expected time to achieve cleanup.

Field tests, such as injection/withdrawal radius of influence tests, are required to determine the spacing of the oxygen delivery systems. Other data required for the design of a bioventing system include the location of potential receptors and logistical information such as availability of utilities and access of the site to personnel.

Although bioventing will not be appropriate at every site, the low operating costs associated with bioventing coupled with its ability to degrade both volatile and nonvolatile contaminants in situ makes bioventing an attractive technology for site managers.

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Bioventing

An Aerobic Process to Treat Vadose Zone Contaminated Soils

Ronald J. Hicks
Groundwater Technology, Inc.
Concord, CA
and
Gregory Sayles and Richard Brenner
Risk Reduction Engineering Laboratory
U.S. Environmental Protection Agency
Cincinnati, OH

Outline

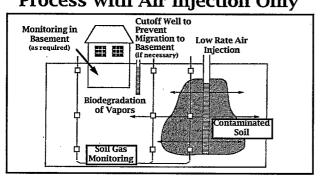
- Fundamentals
- Site Characterization
- Preliminary Design Considerations
- Implementation
- Case Studies
- Cost Comparison

What Is Bioventing?

Definition

Forced air movement through contaminated vadose zone soils to supply the oxygen necessary for otherwise oxygen-limited in situ bioremediation

Conceptual Layout of Bioventing Process with Air Injection Only



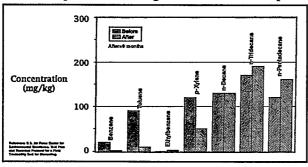
Ability to Control In Situ Environment Vadose Zone

	Ease of Contro		
Parameter	Low	Medium	High
Nutrient Concentration	×		
O ₂ Concentration			×
Cell Concentration	×		
pН	×		
Temperature		×	
Bioavailability	×		
Moisture		×	

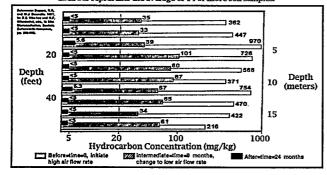
Oxygen Carrier Mass Requirements for Petroleum Biodegradation

Oxygen Carrier	Carrier/Hydrocarbon
Aqueous Solutions Air saturated Nitrate (50 mg/L) H ₂ O ₂ (100 mg/L) Air	400,000 90,000 65,000 13

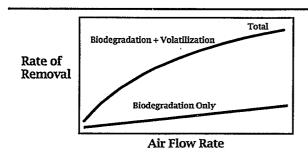
Results of Soil Analysis
Plot V2 at Tyndall AFB before and after venting.
Each bar represents the average of 21 or more soil samples.



Results of Soil Analysis
Building 914 soil samples at Hill AFB before and after venting.
Each bar represents the average of 14 or more soil samples.



Contaminant Removal Biodegradation vs. Volatilization



Advantages of Bioventing

- Employs concentrated source of oxygen
- An in situ technology
- Destroys contaminant
- Treats volatile and nonvolatile contaminants
- Low operating cost

Site Characterization

- **●** Contaminant(s) identity
- Contaminant(s) spatial distribution
- Soil gas survey: O₂, CO₂, TPH

Site Characterization (cont.)

- Nutrients
- pH
- Moisture content
- Cation exchange capacity (CEC)

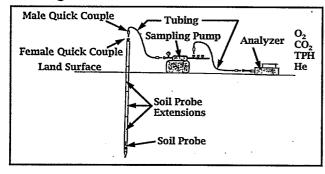
Soil Gas Survey

• Measure

O₂ CO₂ TPH as a function of position in contaminated zone

- Low O₂, high CO₂ indicates
 - Biodegradation activity
 - Oxygen-limited rate
 - Candidate site for bioventing
- \bullet High O_2 , low CO_2 indicates
 - Another factor, e.g., bioavailability, low cell numbers, or nutrients, are limiting the rate
 - Not a candidate site for bioventing

Schematic Diagram of Soil Gas Sampling Using the Stainless Steel Soil Gas Probe



Treatability In Situ Respiration Test

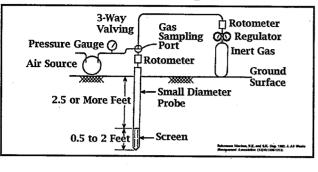
Conduct the following in *contaminated* and in *background* locations:

- 1. Aerate for 1-2 days
- 2. Monitor soil gas until steady state achieved
- 3. Shut off air flow
- 4. Sample soil gas for O₂, CO₂, TPH, and He, with time
- 5. Calculate rate:

Rate ($\%O_2/hr$) = Rate (contaminated)

— Rate (background)

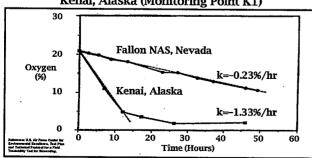
Gas Injection/Soil Gas Sampling Monitoring Point Used by Hinchee et al. (1991) in Their In Situ Respiration Studies



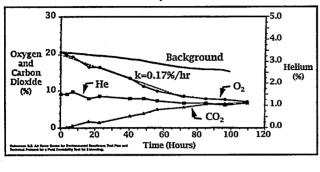
Sample Data Set for Two In Situ Respiration Tests

\cdot	on NAS, Ne Test Well A				i, Alaska Well K1)	
Time (hours)	O ₂ (%)	(%)	Time (hours)	O ₂ (%)	CO ₂ (%)	Helium
-23.5	0.05	20.4	-22.0	3.0	17.5	
0	20.9	0.05	0	20.9	0.05	1.8
2.5	20.3	0.08	7.0	11.0	2.7	1.4
5.25	19.8	0.10	12.25	4.8	4.6	1.4
8.75	18.7	0.13	19.50	3.5	6.0	1.3
13.25	18.1	0.16	26.25	1.8	6.5	1.0
22.75	15.3	0.14	46.00	2.0	7.0	0.9
27.0	15.2	0.22	1			
32.5	13.8	0.14	1			
37.0	12.9	0.23	i			
46.0	11.2	0.22				L Air Force Center for
49.5	10.6	0.16	ľ		and Tackshop	Excellence, Yest Plan Protocol for a Field of for Biowestine.

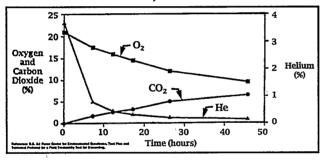
In Situ Respiration Test Results for Two Bioventing Test Sites: Fallon NAS, Nevada (Monitoring Point A2) and Kenai, Alaska (Monitoring Point K1)



In Situ Respiration Test Results for Monitoring Point S1, Tinker AFB, Oklahoma



In Situ Respiration Test Results for Monitoring Point K3, Kenai, Alaska



Biodegradation Rate Calculation

- Assume a stoichiometry, e.g., $C_6H_{14} + 9^1/_2O_2 \longrightarrow 6CO_2 + 7H_2O$
- Calculate conversion factor, e.g.,
 for T=10°C, ∈=0.3
 rate (mg/kg-day)=19.5 rate (%O₂/hr)

Typical Bioventing Rates

• Most sites:

$$Rate = 1-20 \text{ mg/kg-day}$$

i.e., for rate =
$$10 \text{ mg/kg-day}$$

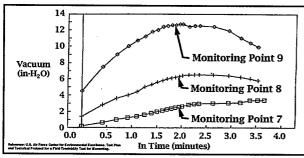
= $3,650 \text{ mg/kg-day}$

Soil Gas Permeability Test

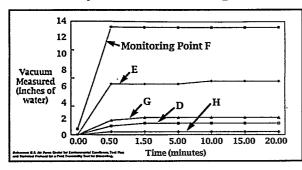
- 1. Initiate air injection
- 2. Measure pressure at monitoring wells at various distances
 - ■With time and/or at steady state
- 3. Use "Hyperventilate" or similar program to determine permeability and radius of influence

K=permeability (cm²=Darcy) R₁=radius of influence (cm)

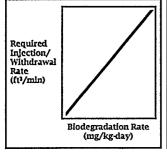
Vacuum vs. In Time Test 2, Bioventing Pilot Test, Site 22-A20, Beale AFB, California

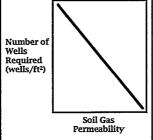


Results of a Field Test to Determine Soil Permeability to Air Flow, k, Sept. 16, 1991



Design Approach





Bioventing for Remediation of Vadose Zone Contamination

Case Study

Initial Conditions

Maximum **Ground Water**

- BTEX^A=2,030 ppb TPH^c as Gasoline=1,800 ppb Concentrations: TOGD=Phase Separated

Hydrocarbons

■ Chlorinated Organics^E=4 ppb

Maximum Soil

- BTEX=420 mg/kg
- TPH as Gasoline=5,200 mg/kg
- Concentrations: Total Oil and Grease=12,000 mg/kg

ABTEX-Benzene, Toluene, Ethylbenzene, and Xylene by EPA Method 602 Modified
BBDL-Below Detection Limits
CTPH-Total Petroleum Hydrocarbons by EPA Method 602 Modified
DTOG-Total Oil and Grease by EPA Method 413.2
FCFU-Colony Forming Units

Initial Conditions (cont.)

Inorganic Concentrations:

- Ammonium, Nitrate, Nitrite, Phosphate=BDL^B
- Potassium=15.7-33.8 ppm

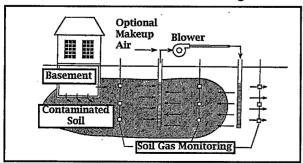
■ pH=6.70-6.90

Bacterial Counts:

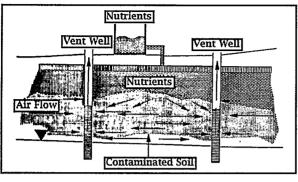
- Hydrocarbon Utilizers= 3.1x10³-1.7x10⁵ CFU^F/mL
- **■** Background Heterotrophs= 1.2x105-6.9x105 CFU/mL

ABTEX-Benzene, Toluene, Ethylbenzene, and Xylene by EPA Method 602 Modified BBDL-Below Detection Limits CPHH-Total Petroleum Hydrocarbons by EPA Method 602 Modified PTOG-Total Oll and Grease by EPA Method 413.2 *Analysis by EPA Method 602 *CFU-Colony Forming Units

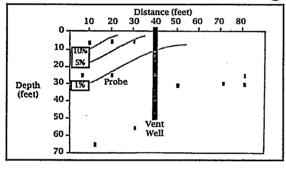
Conceptual Layout of Bioventing Process with Soil Gas Reinjection



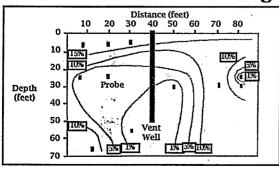
Soil Vent Bioremediation System



Oxygen Concentration in Vadose Zone Before Venting



Oxygen Concentration in Vadose Zone After Venting



Injection vs. Withdrawal

Advantages	Disadvantages		
Inje	ection		
No off-gas treatment Long gas residence time Deep sites	Need extensive soil gas monitoring Near receptors Shallow sites Less control of gas flow		

Withdrawal

Little soil gas monitoring needed
Can monitor off-gas
Shallow sites
Greater control of gas flow

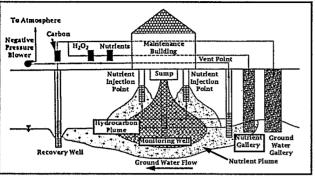
Initial Conditions

- Contaminant
 - High M.W. petroleum hydrocarbons in unsaturated zone
 - Initial mass estimated at 11,000 kg
- Geology
 - Alluvial sands and gravels

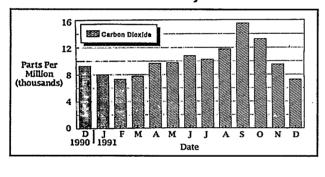
Initial Conditions (cont.)

- Treatability results indicated significant biodegradation with aeration
- Vapor extraction pilot test indicated 50' ROI





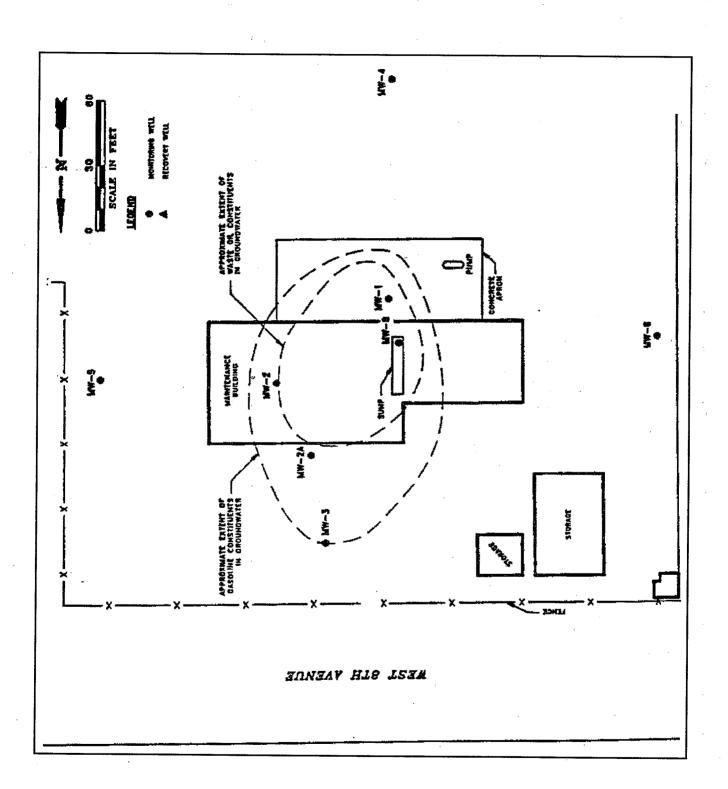
Carbon Dioxide from Vapor Extraction System

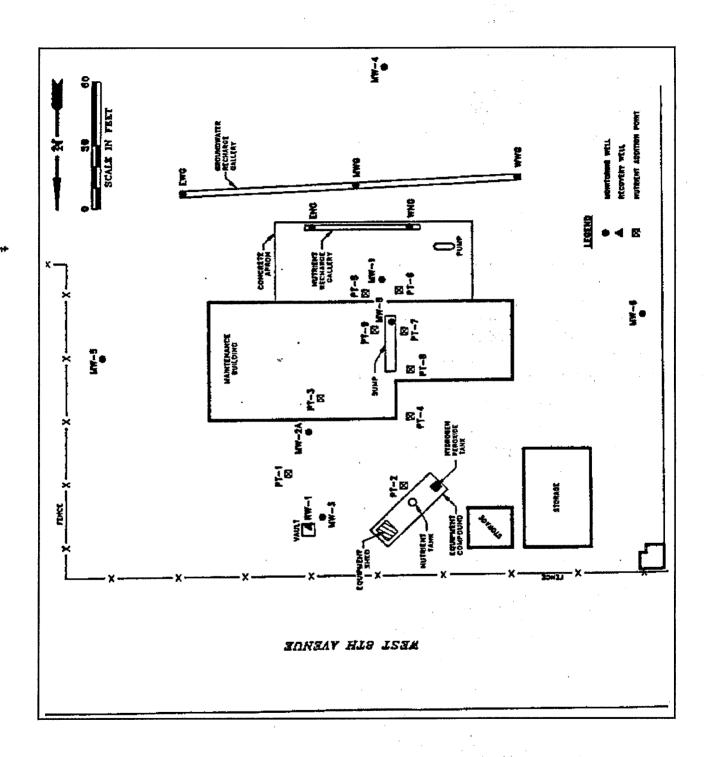


Carbon Isotope Analysis

Sample Location	CO ₂ (%)	δ ¹³ C	δ ¹³ C
Vapor extraction	1.27	-26.37	-24.3 to -30.1
MW-9	0.052	-18.14	-18.1 to -24.4

Reference; Aggerned and Marches, 1981, Dayleyane Schools Technology 28:1179-1160.





Results

- 353 kg volatilized
- Approximately 15,104 kg removed biologically (including saturated phase)

Results (cont.)

- δ¹³C values suggested hydrocarbons were the main source of CO₂
- •Site remediated in approximately 3 years at a total cost of approximately \$500,000.00

Remediation Results

Process	Mass Removed
Phase separated product recovery Volatilization Biodegradation ^A Total	1,510 lbs 780 lbs 33,300 lbs 35,590 lbs
Total ground water recovered and reinjected	8,835,598 gal (≥15 pore volumes)
Initial Contaminant Mass Estimate *Estimated from CO ₂ measurements from the vapor extraction.	25,800 lbs

*Estimated from CO₂ measurements from the vapor extraction system effluent. CO₂ measurements were converted into contaminant mass removal rates using the following conservative assumption.

native organic matter.

2. Forty percent of the biodegraded organic carbon was evolved as carbon disside

Platerence: Helison, C.H., R.J. Hicks, and S.D. Andreurs. 1993. In altu bil premed at on; on integrated approach. in: J.H.

Cost/Performance Comparison for Various Oxygen Systems High Degree of Contamination

Costs System	Cap	ital	Operation	М	aintenance
Air sparging	\$35	000	\$800/mont	h \$1.	,200/month
Water injection	\$77	000	\$1,200/mont	h \$1	,000/month
Venting system	\$88	500	\$1,500/mont	h \$1	000/month
Peroxide system	\$60	000	\$10,000/mont	h \$1	500/month
Nitrate system	\$120	000	\$6,500/mont	h \$1	,000/month
Performance					
System	lbs/day oxygen	% site treated	Utilization efficiency %	Time of treatment	\$/lb oxygen used
Air sparging	6	41	70	858 days	\$25.80
Water injection	8	75	50	1,580 days	\$28.62
Carrellana anantama	4.000	60	5	132 days	\$3.82
vening system				220 4	610.00
Venting system Peroxide system	190	100	15	330 days	\$18.60

SUBSURFACE BIOREMEDIATION

John T. Wilson, Don K. Kampbell, Steven R. Hutchins Robert S. Kerr Environmental Research Laboratory U.S. Environmental Protection Agency Ada, OK

and

Daniel F. Pope
Dynamac Corporation
Robert S. Kerr Environmental Research Laboratory
Ada, OK

SITE CHARACTERIZATION

Most commonly, a plume of contaminated ground water originates in a spill of a nonaqueous phase liquid (NAPL) such as gasoline, diesel oil, or jet fuel. A small fraction of the total contaminant mass exits in the ground water. As a result, monitoring wells greatly underestimate the mass of contaminant subject to remediation.

At present, the acquisition, extraction, and analysis of core samples is the only technique available to quantify the mass of an NAPL contaminant in the subsurface. Soil gas screening techniques can locate the spill both horizontally and vertically. Then a continuous series of core samples should be taken across the entire interval contaminated with NAPL. Cores should be extracted in the field, rather than shipped back to the laboratory for extraction.

In addition to the location of the NAPL source area, design or evaluation of subsurface bioremediation requires information on lithology of the site and the local pneumatic or hydraulic conductivity. This information traditionally is obtained by coring a site and conducting aquifer tests in wells. Cone penetrometers are developing as a rapid and inexpensive alternative to traditional techniques. They can rapidly and accurately map lithological features and determine local hydraulic conductivity. Hydraulically driven soil gas samplers also are gaining wide application. They greatly reduce the labor involved in soil gas sampling and allow sampling at greater depth.

The role of site characterization is illustrated in a case study. A spill from an underground storage tank was flushed with hydrogen peroxide and mineral nutrients for 3 years. When the concentration of benzene, toluene, ethylene, and xylene (BTEX) compounds in monitoring wells

approached acceptable levels, the site owner petitioned for closure. Significant concentrations of alkylbenzenes (BTEX) remained in core material after remediation; ground water moving past the spill, however, was not contaminated. Apparently, the residual contamination was sequestered in material that was not permeable to water.

NATURAL (INTRINSIC) BIOREMEDIATION

Intrinsic bioremediation is an important process for destruction of contaminants in the subsurface. It deserves to be considered as part of the comprehensive plan to manage contaminants at hazardous waste sites. At present, intrinsic bioremediation suffers from a lack of regulatory credibility, largely because of inadequate or incomplete site characterization and laboratory studies.

A complete assessment of intrinsic bioremediation includes the following activities:

- 1. Locate areas with oily-phase contamination.
- 2. Determine the trajectory of ground water flow.
- 3. Install monitoring wells along the plume.
- 4. Determine the apparent attenuation along the plume.
- 5. Correct apparent attenuation for dilution and sorption.
- 6. Assume corrected attenuation is bioattenuation.
- 7. Confirm bioattenuation from the stoichiometry of electron acceptors and donors.
- 8. Estimate the elapsed time to monitoring wells.
- 9. Calculate rate constants from the elapsed time and bioattenuation.
- 10. Confirm rates with laboratory microcosms.
- 11. Extrapolate extent of bioattenuation to the point of compliance to determine if the extent of bioattenuation is protective.

AIR SPARGING OR BIOSPARGING

Air sparging or biosparging refers to the technique of injecting air below the water table. The name implies that the technique works by enhanced dissolution of the NAPL into the sparged air. Actually, the technique is an effect mechanism to oxygenate ground water in contact with the NAPL. Most of the removal is due to aerobic biodegradation of the NAPL.

Biodegradation supported by sparging can remove BTEX compounds from ground water and NAPLs quickly. After the aromatic compounds are removed, residual hydrocarbons might be persistent.

Air sparging is not appropriate for every site, and it must be managed carefully. After contact with the NAPL, the sparged air often exceeds the lower explosive limit and can be a hazard in confined spaces.

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SUBSURFACE BIOREMEDIATION

John T. Wilson, Steven R. Hutchins, and Don H. Kampbell, U.S. Environmental Protection Agency

Daniel Pope, Dynamac Corporation

R.S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, Ada, OK

NEW APPROACHES FOR SITE CHARACTERIZATION

DEFINITION OF THE PROBLEM

NONAQUEOUS PHASE LIQUIDS NAPLS, LNAPLS, DNAPLS

The NAPLs define the source area of the ground water plume.

To the extent feasible, these materials should be removed by free product recovery, before bioremediation proceeds.

SITE CHARACTERIZATION REQUIREMENTS SPECIFIC TO THE SUBSURFACE

Goals:

Map the contaminant mass in three dimensions.

Determine the co-distribution of contaminant and hydraulic or pneumatic conductivity

PROBLEMS WITH MONITORING WELLS

They cannot estimate contaminant mass in NAPLs

They cannot estimate contaminant mass adsorbed to solids

They do not sample contaminant mass above the water table.

COMPARISON OF CONTAMINANT MASS IN GROUND WATER TO TOTAL CONTAMINANT MASS

At a Pipeline Spill in Kansas:

Mass ir	ı	Mass	in
Ground	Water	Subsu	ırface

Benzene	22	kg	320	kg
BTEX	82	kg	8,800	kġ
TPH	115	kg	390,000	kg

WHEN TOTAL CONTAMINANT MASS IS UNKNOWN

Cannot estimate requirements for electron acceptors.

Cannot estimate requirements for nutrients.

Cannot determine time required for cleanup.

RELATIONSHIP BETWEEN FREE PRODUCT IN MONITORING WELLS AND CONTAMINANT MASS IN AQUIFER

Position and quantity in wells does not relate to position and quantity in aquifer.

Amount of free product related to location of water table.

RELATIONSHIP BETWEEN FREE PRODUCT IN MONITORING WELLS AND CONTAMINANT MASS IN AQUIFER

Free product is greatest when water table is low.

Free product can disappear when water table is high.

DRILLING AND SAMPLING TECHNIQUES

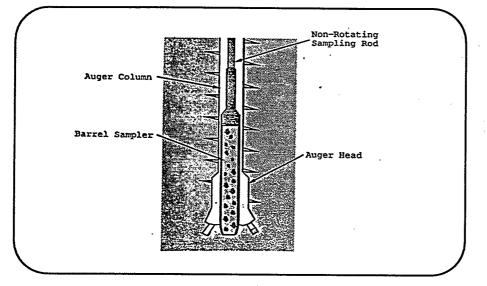
Conventional techniques
Hollow-stem augers
Split-spoon samplers

New techniques Cone penetrometer Geoprobe

STATE OF PRACTICE FOR DETERMINING CONTAMINANT MASS

Subsample cores in the field for extraction and analysis of specific contaminants and total petroleum hydrocarbons.

Cores can be screened with a hydrocarbon vapor analyzer.



CONE PENETROMETERS

Advantages:

Fast and relatively inexpensive.
Measure properties on an appropriate scale.

Disadvantages:

Don't work well in geological materials with boulders or cobbles.

Restricted to shallow depths.

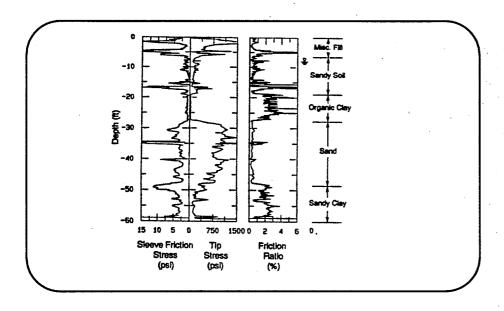
INFORMATION PROVIDED BY CONE PENETROMETERS

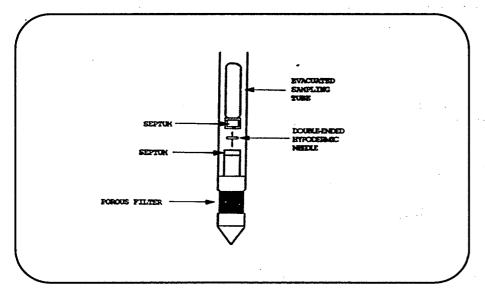
Lithology inferred from tip and sleeve resistance.

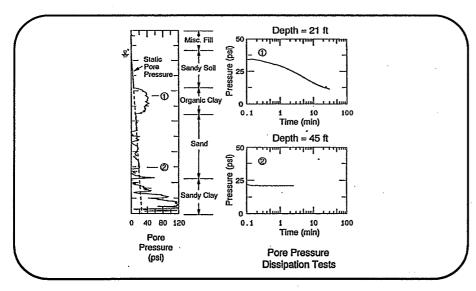
Electrical conductivity.

Water samples for analysis of contaminants.

Local hydraulic conductivity.







GEOPROBE

Advantages: Very fast and inexpensive Leaves a small borehole

Disadvantages:
Restricted to shallow unconsolidated materials.
Does not give information on lithology.

INFORMATION PROVIDED BY A GEOPROBE
Soil gas samples for analysis.
Water samples for analysis.
Small core samples for analysis.

CASE STUDY

Application of site characterization techniques to evaluate subsurface bioremediation.

WHAT CAN BIOREMEDIATION ACHIEVE?

Remove all components of a spill from the subsurface?

Remove hazardous components of a spill from the subsurface?

WHAT CAN BIOREMEDIATION ACHIEVE?

Remove hazardous components of a spill from ground water?

Remove hazardous components from pumped ground water?

CASE STUDY

Spill of oily liquids from a temporary underground holding tank

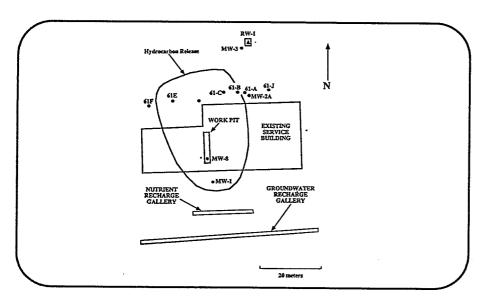
Shallow water table aquifer in an industrial area

Fluvial depositional environment.

TECHNOLOGY IMPLEMENTED

Ground water was circulated in a closed loop.

Added hydrogen peroxide, ammonia-N, and phosphate from 7/89 to 3/92.

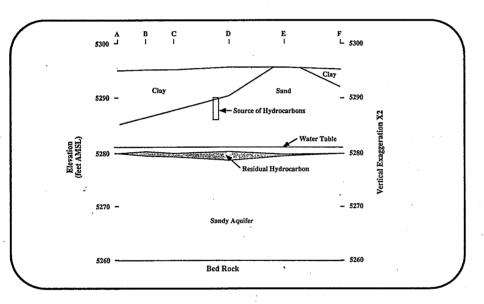


Reduction of Benzene in Ground Water

Well	Before	During	After	
	-(ug/	-(ug/liter)		
MW-1	220	<1	<1	
MW-8	180	130	16	
MW-2A	?	11	0.8	
MW-3	11	5	2	
RW-1	<1	2	<1	

Reduction of BTEX in Ground Water

Well	Before	During	After	
	-(ug/liter)			
MW-1	2,030	164	<6	
MW-8	1,800	331	34	
MW-2A	?	1,200	13	
MW-3	1,200	820	46	
RW-1	<1	2	<1	



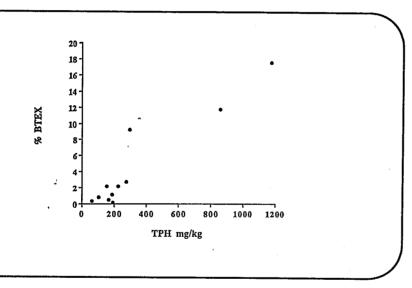
Concentration of Contaminants Remaining at Most Contamined Level

Bore	TPH	BTEX	Benzene		
	(mg/kg)				
В	1,767	0.8	<0.2		
С	156	3.5	<0.2		
D	1,180	260	4.3		
Е	156	3.5	0.06		

RELATIONSHIP BETWEEN GROUND WATER AND OILY PHASE CONTAMINATION

The reduction in concentration in ground water equivalent to the reduction in weathered oil.

Not all the oily phase weathered. Is it in contact with ground water?



RELATION BETWEEN PUMPED WELLS AND PASSIVE MONITORING WELL

Why didn't the pumped well RW-1 contain contaminants?

How can we estimate the effects of dilution in pumped well?

WILL A PLUME OF CONTAMINATED GROUND WATER RETURN?

Is the electron acceptor supply greater than the demand?

What is mass transfer from residual oily phase to moving ground water?

Potential Oxygen Demand

Bore	Above	Within	Below
	(mg O ₂ /kg day)		
A		15.5	6.0
В		>30	<3
С	<4	>36	5.7 ·
D			7:3
E	7.4	>34	
F		23.5	21.0

Conditions during Active Remediation

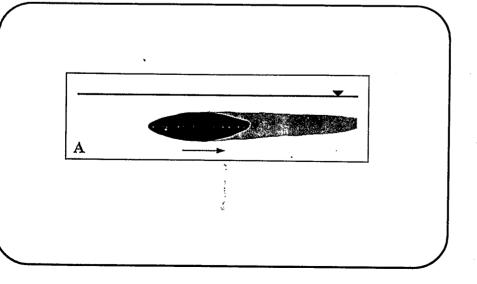
Parameter	Active Remediation
dissolved oxygen	470 mg/liter
hydraulic gradient	0.097 m/m
ground water flow	2.4 m/day .
travel time	20 days
BOD supported	20 mg/liter day

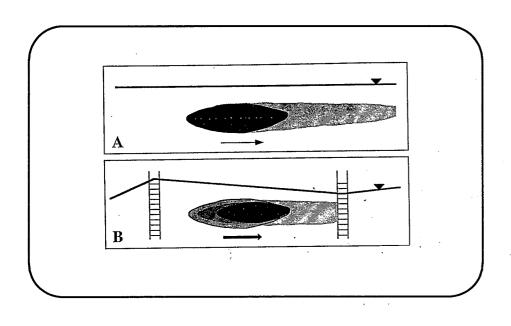
Conditions after Active Remediation

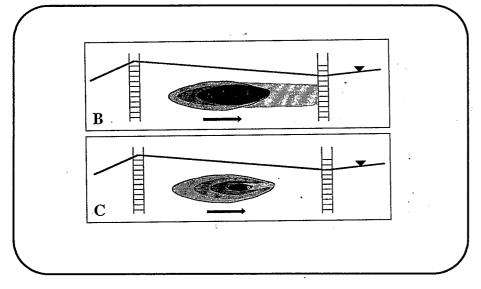
Parameter	Active Remediation	
dissolved oxygen	5.5 mg/liter	
hydraulic gradient	0.0012 m/m	
ground water flow	0.3 m/day	
travel time	1,500 days	
BOD supported	0.004 mg/liter day	

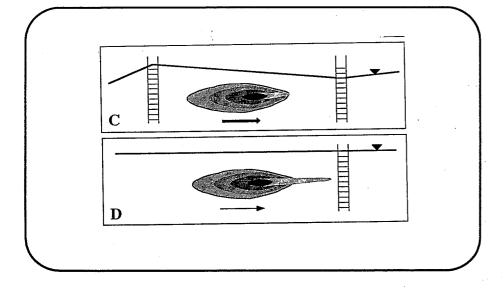
Contrast Before and After

Active	Afterwards
470 mg/liter	5.5 mg/liter
0.097 m/m	0.0012 m/m
2.4 m/day	0.03 m/day
20 days to RW-1	1,500 days to monitoring
20 mg/liter day	0.004 mg/liter day









WILL THE PLUME RETURN? TOO CLOSE TO CALL!

How long would it take for a plume to develop and reach the monitoring wells?

WILL THE PLUME RETURN?

How long will it take water to move all the way across the spill to the monitoring well under ambient conditions?

WILL THE PLUME RETURN?

Has active treatment weathered the spill to the point that intrinsic bioremediation prevents development of a plume?

NATURAL OR PASSIVE BIOREMEDIATION

The preferred description is INTRINSIC BIOREMEDIATION

All bioremediaton is "natural."

Neither the microorganisms nor the microbiologists are "passive."

INTRINSIC BIOREMEDIATION

Determination is site specific.

Requires extensive site characterization.

Burden of proof is on the proponent, not the regulator.

PATTERNS OF INTRINSIC BIOREMEDIATION

Limited by supply of a soluble electron acceptor.

Aerobic Respiration

Nitrate Reduction

Sulfate Reduction

PATTERNS OF INTRINSIC BIOREMEDIATION

Limited by biological activity.

Iron Reduction

Methanogenesis

Sulfate Reduction

PATTERNS OF INTRINSIC BIOREMEDIATION Limited by supply of electron donor.

Reductive Dechlorination

INITIAL ELEMENTS OF A QUANTITATIVE ASSESSMENT OF INTRINSIC BIOREMEDIATION

- Locate areas with oily phase contamination.
- 2) Determine trajectory of ground water flow.
- 3) Install monitoring wells along plumes.

ADDITIONAL ELEMENTS OF A QUANTITATIVE ASSESSMENT

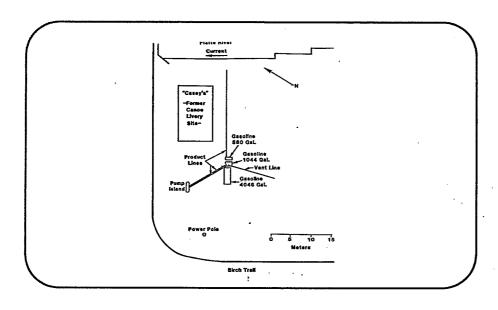
- 4) Determine apparent attenuation along plumes.
- 5) Correct apparent attenuation for dilution or sorption.
- 6) Assume corrected attenuation is bioattenuation.
- 7) Confirm bioattenuation from stoichiometry of electron acceptors or donors.

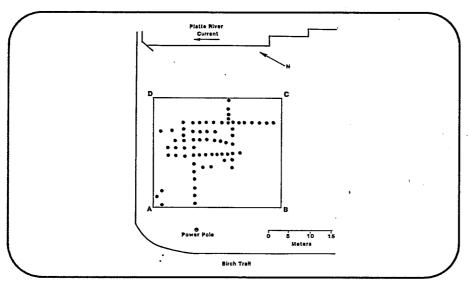
FINAL ELEMENTS OF A QUANTITATIVE ASSESSMENT

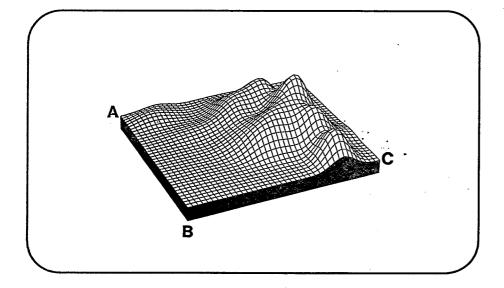
- 8) Estimate elapsed time to monitoring wells.
- 9) Calculate rate constants from elapsed time and bioattenuation.
- 10) Confirm rates with laboratory microcosms.

CASE STUDY OF INTRINSIC BIOREMEDIATION

SLEEPING BEAR DUNES NATIONAL LAKE SHORE







LOCATE AREAS WITH OILY PHASE MATERIAL

Plumes usually do not attenuate in the presence of oily phase contamination.

Goal is to determine the boundary of oily phase contamination.

LOCATE AREAS WITH OILY PHASE MATERIAL

Often can be conveniently located by a soil gas survey.

Confirm with core analysis.

DETERMINE TRAJECTORY OF GROUND WATER FLOW

The direction of flow controlled by the hydraulic gradient measured from water table elevations.

The velocity of flow is the product of the hydraulic gradient and the hydraulic conductivity as determined through an aquifer test.

VARIATION IN GROUND WATER FLOW

Most plumes vary in direction and velocity of flow.

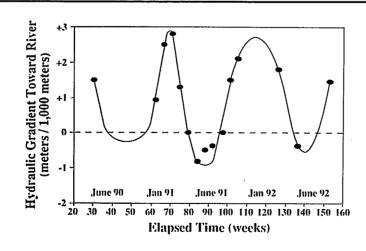
Plumes in upland landscapes tend to be less variable.

VARIATION IN GROUND WATER FLOW

Plumes near rivers or estuaries tend to be more variable.

At a minimum, quarterly monitoring for a year is required.

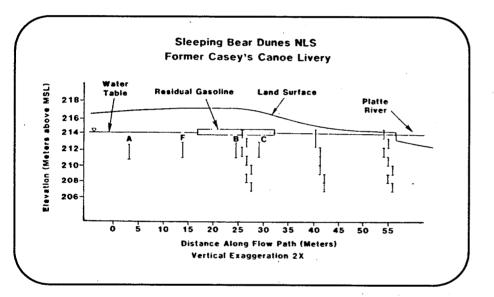
Several years of monitoring is better.

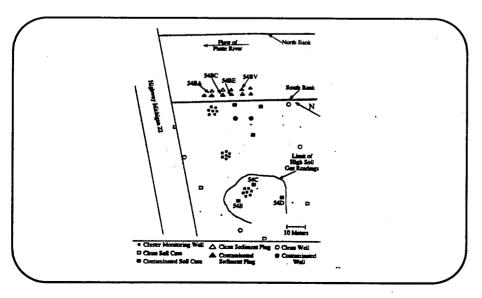


INSTALLATION OF MONITORING WELLS

Wells should be installed along a flowpath near the centerline of the plume.

Wells should be installed across the vertical extent of the plume.





VERTICAL DISTRIBUTION OF MATERIALS IN GROUND WATER SEVENTY FEET DOWN GRADIENT OF THE SPILL AREA

Elevation AMSL	Total BTEX	Methane	Oxygen
(feet)		(mg/liter)	
587- 584	0.17	1.55	0.8
584-581	2.0	3.1	0.4
581-578	0.041	0.56	0.7
578- 575	0.086	0.47	0.7
5 75-572	0.037	0.087	0.5
572-569	0.00006	0.035	0.7
569-566	0.00006	0.0006	1.3

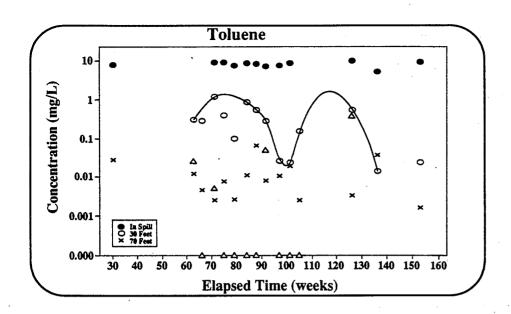
VERTICAL DISTRIBUTION OF MATERIALS IN GROUND WATER SEVENTY FEET DOWN GRADIENT OF THE SPILL AREA

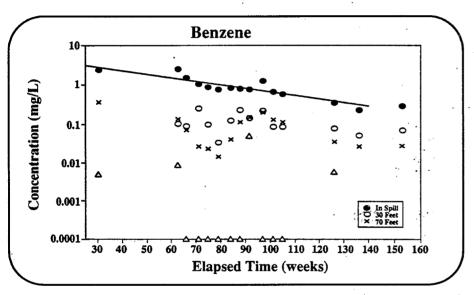
Elevation AMSL	Total BTEX	Nitrate	Sulfate	Iron II
(feet)		mg	/liter	
587-584	0.17	< 0.05	4.8	3.3
584-581	2.0	0.10	< 0.05	5.2
581-578	0.041	< 0.05	8.9	5.1
578-575	0.086	0.2	18.4	3.0
575-572	0.037	· 0.2	16.2	0.17
572-5 69	0.00006	0.4	12.9	0.05
569-566	0.00006	< 0.05	6.0	0.05

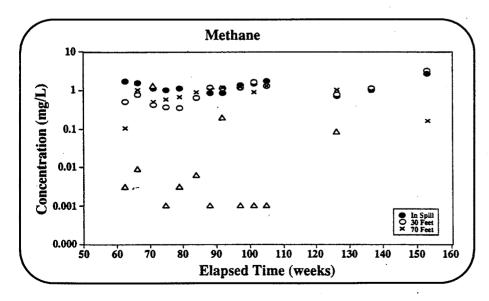
DETERMINE APPARENT ATTENUATION

Collect monitoring data over time to estimate apparent attenuation.

Apparent attenuation usually has a strong contribution from simple dilution and sorption.







CORRECTING ATTENUATION FOR DILUTION OR SORPTION

Identify a component of the plume that can serve as a tracer.

A GOOD TRACER

-is not biodegradable in the absence of oxygen.

A GOOD TRACER

-is present in the plume
 source area at concentrations
 at least 100 times
 its detection limit.

A GOOD TRACER

-has the same sorptive properties as the regulated compounds.

Apparent Attenuation of 2,3-Dimethylpentane in the Plume of Contaminated Ground Water

Date	In Spill	30 feet	70 feet
	(ug/liter	averaged ove	er 21 feet)
7/92	23.4	7.30	1.64
11/92	26.6	6.24	1.77

CORRECTING ATTENUATION FOR DILUTION OR SORPTION

To correct apparent attenuation for dilution or sorption, divide the concentration of contaminants by the concentration of the tracer.

STOICHIOMETRY OF ELECTRON ACCEPTORS AND ELECTRON DONORS

After correction for dilution, the concentration of biodegradation end products should balance the concentration of organic materials destroyed.

Methane Production and Electron Acceptor Consumption in the Most Contaminated Interval

Compound	Up Gradient	Down Gradient	BTEX Consumed	
	(mg/liter)			
Methane	0.08	29.8	39	
Nitrate-N	15.3	<0.05	14	
Sulfate	20.0	<0.05	4.2	
Iron II	3.5	27.8	1.1	
Oxygen	2.4	<0.1	0.8	

Forty-two mg/liter BTEX was actually consumed.

STOICHIOMETRY OF ELECTRON ACCEPTORS AND ELECTRON DONORS-SOURCES OF ERROR

Methane might be lost to volatilization.

Iron may precipitate as iron (II) sulfide or iron (II) carbonate.

Natural organics may exhibit an electron acceptor demand.

CALCULATING RATE CONSTANTS

When limited by biological activity, rates are apparently pseudo-first order on time.

When limited by supply of electron acceptor, rates are apparently pseudo-first order on length of travel, which often is proportional to time.

ESTIMATING ELAPSED TIME

Determine the time of travel from the edge of the oily phase material to the monitoring well, or from well to well along a flow path.

ESTIMATING ELAPSED TIME

Calculate elapsed time from the flow velocity as predicted from the hydraulic gradient and hydraulic conductivity, or conduct a tracer test.

LABORATORY CONFIRMATION

When bioremediation is limited by biological activity, it is often possible to duplicate the kinetics of degradation in the laboratory.

LABORATORY CONFIRMATION

If bioremediation is limited by the supply of electron acceptor, laboratory kinetics grossly overestimate field kinetics.

COMPARISON OF FIELD AND LABORATORY MICROCOSM RATE CONSTANTS

Distance from spill	Benzene	Toluene	Ethyl- benzene
(feet)	percen	t depleted [er week
Field rate,	corrected fo	r dilution o	or sorption
30	- 0.6	42	4.6
70	0.9	17	5.2
Laboratory losses, after		ıs, correcte	d for abiotic
0	0.1	30	0.2
30	- 0.4	6.2	0.7
70	- 0.1	7.9	10

COMPARISON OF FIELD AND LABORATORY MICROCOSM RATE CONSTANTS

from spill	Toluene	m+p- Xylene	o-Xylene
(feet)	percent	depleted	per week
Field rate,	corrected f	or dilution	or sorption
30	42	5,9	8.5
70	17	4.2	5.3 .
Laboratory losses, after		ns, correc	ted for abiot
. 0	30	0.2	< 0.1
30	6.2	0.7	0.8
70	7.9	0.3	0.4

COMMON ERRORS IN ESTIMATES OF INTRINSIC BIOREMEDIATION

Oxygen is the only electron acceptor considered.

The contaminant being modeled is the only electron donor considered.

AIR SPARGING AND BIO-SPARGING

Air Sparging and Bio-sparging are the most rapidly growing applications of subsurface bioremediation.

The Problem

• Contaminants below the water table

Contaminants below the water table

- Pump & Treat ineffectual low solubility of oily phase
- Less than 5% ever enters solution
- Remainder sorbed to solids or free phase

Contaminants below the water table

- Soil Venting ineffectualwater saturated pores
- Bioremediation costly with hydrogen peroxide

Soil Vapor Extraction

- Indirectly stimulate biodegradation of dissolved contaminants
- Increased oxygen content in vadose zone
- Increased diffusion from vadose zone to GW

Soil Vapor Extraction

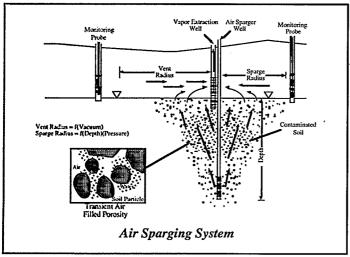
- Direct treatment of saturated zone contaminants
- Generally requires that site be effectively dewatered so air flow can be induced

Need for efficient, inexpensive delivery of oxygen to saturated zone

AIR SPARGING

Air Sparging

- Injection of air under pressure below the water table
- Creates transient air filled porosity



- Minimum pressure to displace water
- That needed to overcome resistance of soil matrix to air flow

Pressure Required

- Function of water column height to be displaced
- Flow restriction (air/water permeability) of soil matrix

Pressure Required

- When "break-out" pressure achieved
- Air enters the soil matrix
- Travels horizontally/vertically through soil, displacing water
- Exits into vadose zone

- Enhances biodegradation by increasing oxygen transfer
- Enhances physical removal by volatile (vapor phase) extraction

Air Sparging

Can treat volatiles/organics in GW aquifers by volatile removal, biodegradation

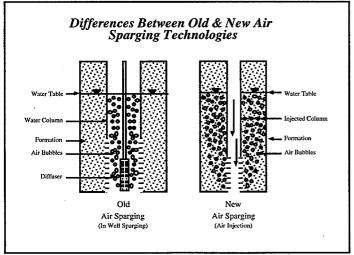
Air Sparging

- Extensively used in Germany since 1985
- Successfully introduced in the US in 1990

- Earlier systems injected air into water column in well
- No direct contact with formation matrix

Air Sparging

- Now, injection pressure > hydraulic head
- Well contains no water
- Air directly injected into formation



Effects of Air Sparging

- Enhanced oxygenation
- Enhanced dissolution
- Volatilization
- GW stripping
- Physical displacement of GW

Enhanced Oxygenation

- Replenishes oxygen depleted by chemical/biological processes
- Normal replenishment relies on diffusion from water table surface
- Sparged air, distributed throughout aquifer, has short diffusion path
- Enhanced oxygenation stimulates biodegradation

Enhanced Dissolution

- Injected air causes turbulence in pores
- Mixes water, adsorbed contaminants
- Enhances partitioning into water
- Normal water/soil contact static, dissolution diffusion limited

Enhanced Dissolution

- Enhanced dissolution beneficial if GW collected
- Detrimental if contaminants not captured, treated by in-situ stripping
- Dissolution can help promote biodegradation

Volatilization

- Adsorbed contaminants evaporate into air stream
- · Carried into vadose zone
- Extent of volatilization governed by vapor pressure

Volatilization

- Prevented in saturated zone no air phase
- Can remove significant mass of contaminants

 $s_k = s_k = \left(s_k \left(\frac{\delta_k}{\delta_k} \right) + s_k \left(\frac{\delta_k}{\delta_k} \right) \right)$

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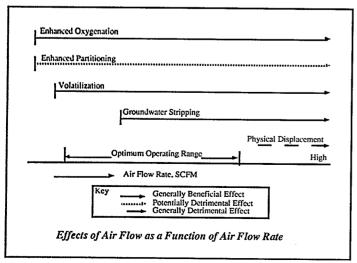
the progression will be a con-

Ground Water Stripping

Volatiles with high Henry's Law Constant volatilize from water into air stream, removed

Physical Displacement

- Water can be rapidly displaced at very high air flow rates
- Observed in air-rotary drilling
- Contaminated displaced water spreads contamination in any direction
- May not be captured by existing GW systems



Air Flow Rates

- Too low air flow will not effectively remove volatiles
- May increase ground-water concentrations
- Too high flow can spread contamination
- Optimizing air flow will maximize mass removal, minimize potential contaminant spread

Comparison Of Air Sparging To Other Sources Of Oxygen

- Soil Venting Low contact
- Injected Peroxide -Expensive, unstable

OXYGEN AVAILABILITY, LB/DAY

	Air Sparg	ļing		Hydrogen Peroxide (1000 ppm)			
Flow		Utilization		Flow	Utilization	1 .	
SCI*M	100%	50%	10%	GPM	100%	50%	107
10	236	118	24	10	56	28	6
25	590	295	59	2	140	70	14
50	1182	590	118	50	280	140	28

Removal Of Contaminants In Air From Soil Matrix

> 1 mm Hg vapor pressure

Removal Of Contaminants In Air From GW

Henry's Law constant [KH (atm-m³-mole ⁻¹)] greater than 10⁻⁵

HENRY'S CONSTANT FOR SELECTED HYDROCARBONS

Constituent

	(atm-m3-mole-1)
Cyclohexane	1.9 x 10 ²
Benzene	5.6 x 10-3
Ethylbenzene	8.7 x 10-3
Toluene	6,3 x 10 ⁻³
Xylene	5.7 x 10 ⁻³
Naphthalene	4.1 x 10-4
Phenanthrene	2.5 x 10-5

Primary And Secondary Removal Mechanisms

SITE AND PILOTTEST DATA NEEDED FOR DESIGN

Data

Impact on Design

Lithological Barriers
Vertical Extent of Contamination
Horizontal Extent of Contamination
Volatility of Contaminant
Sparge Radius of Influence
Optimal Flow Rates
Vent Radius of Influence
Vacuun/Pressure Balance
Vapor Levels

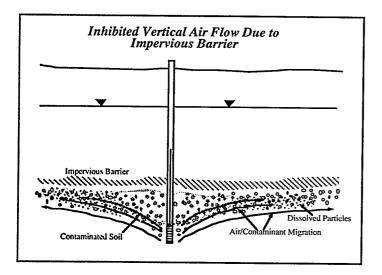
Feasibility/Sparging Depth Sparging Depth Number of Sparge Wells Vapor Control (Venting) Well Spacing/Flow Requirement Compressor Size Well Spacing Blower Size/Well Placement Vapor Treatment

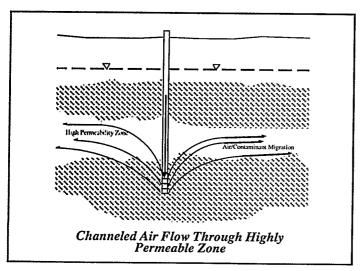
Air Sparging Disadvantages

- Flow away from injection point
- Hard to maintain control

Air Flow Paths

- Injected air travels horizontally, vertically
- Flow impedance by lithological barriers blocking vertical air flow
- Channelization horizontal air flow captured by high permeability channels
- Small permeability differences can change flow paths





Air Flow Paths

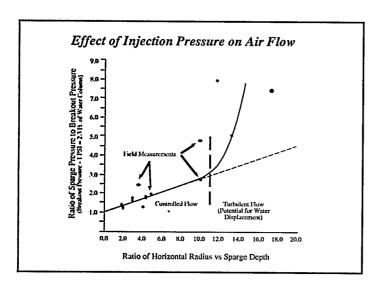
- Channeled air flow may cause uncontrolled spread of contamination
- Lithological profile should be developed before system installed
- Pilot test

Spreading of Dissolved Contaminants

- Injection pressure, flow
- Water table mounding

Injection Pressure

- Minimum pressure must overcome water column pressure
- 1 psi for every 2.3 feet of hydraulic head
- Above minimum, water injected into aquifer



Water Table Mounding

- Air sparging raises water table
- GW flows away from mound

Water Table Mounding

- Mounding produced by sparging caused by displacement of water with air
- Flow away from mound may not be induced because net density of water column is decreased
- Contaminants may be stripped before significant migration

WATER TABLE MOUNDING AND COLLAPSE

Depth to V	Vater (ft) @				
Well # -	Distance from Sparge Point	Statīc Water Level	Sparging Water Level	5 Min After	10 Min After
MW-7	5	6.46	4.09	10.03	6,96
SE-1919	6.42	6.20	6.93	6.54	
S-2629	6,71	6.55	6,96	6.77	
NE-13	13	6.52	6.11	7.44	6.75

Accelerated Vapor Travel

- To basements, other low pressure areas
- Use vent system to capture vapors

Ground Water Chemistry

- Oxidize Fe, Mn
- CO₂ may precipitate CaCO₃

Summary

Applicable Contaminants

- Volatile, relatively insoluble
- Removal as vapor

Applicable Contaminants

- Biodegradable
- Removal by biodegradation

Geology of Site

- Relative homogeneity
- Strata above sparging point > permeability

Geology of Site Permeability

- Ratio of horizontal to vertical permeability
- <2:1 OK, even if permeability relatively low
- $(>10^{-5} \text{ cm/sec})$

Geology of Site Permeability

- If H:V > 3:1
- Permeability should be >10⁻⁴ cm/sec

Sparge System Depth

- Minimum depth 4 feet
- Saturated thickness required to force cone-out from injection point

Sparge System Depth

- Maximum depth 30 feet
- Difficult to predict flow paths
- Small permeability differences create major variations
- Difficult to contain/capture sparged air

Sparge System Depth

- Sufficient unsaturated zone depth for SV
- > 4 feet to water table

Site Characterization Contaminant Mass Distribution

- Vertical for location of sparging points
- Horizontal for complete coverage
- Downgradient plume for monitoring, remediation

Site Characterizaton Potential Receptors

- Soil venting for vapors
- GW extraction/barriers for dissolved contaminants

Pilot Tests

- Air sparging radius of influence
- Soil venting radius of influence*
- Combined sparge/vent test*
 - *Where vapors are a concern

Pilot Test Measurements

- Vacuum/pressure vs.distance
- Volatile concentrations
- Carbon dioxide/oxygen levels
- DO levels in GW
- Water levels

Volatile Concentrations

Which compounds removed

Carbon Dioxide/ Oxygen Levels

- Indicator of biological activity
- Before, during, after pumping

Carbon Dioxide/ Oxygen Levels

- Usually depressed O₂, elevated CO₂ before
- Rise during test indicates effectiveness
- Drop after test indicates biological activity rates

Dissolved Oxygen In GW

- Indicator of sparging effectiveness
- Often < 2 mg/l in contaminated zone

Water Levels

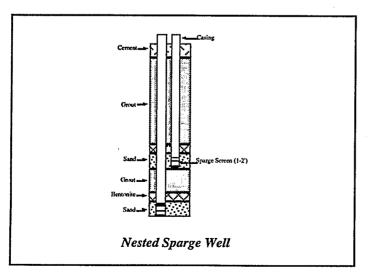
Mounding effect

Air Sparging Systems

- Well
- Compressor/Blower
- Monitoring System
- Heat Exchanger
- SVE System
- Vapor Treatment
- GW Control

Air Sparging Well

- 10-15 ft intervals
- Steel, above 15 psi



Compressor/Blower

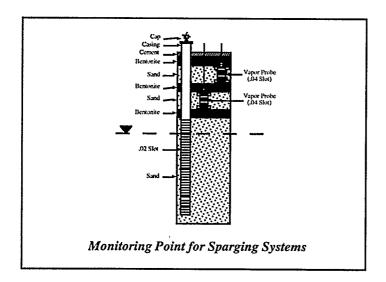
- 10-20 cfm/well
- 1-3 X breakout pressure
- Air:water 10-20:1

Filter

Remove oil, particulates, moisture

Monitoring System

- Well to measure water table elevation
- DO, contaminants, pressure
- Vapor probes for volatiles, pressure/vacuum



Heat Exchanger

For PVC systems

Soil Vacuum System

- To capture volatiles
- Maintain net negative pressure
- Total flow 2X sparge flow

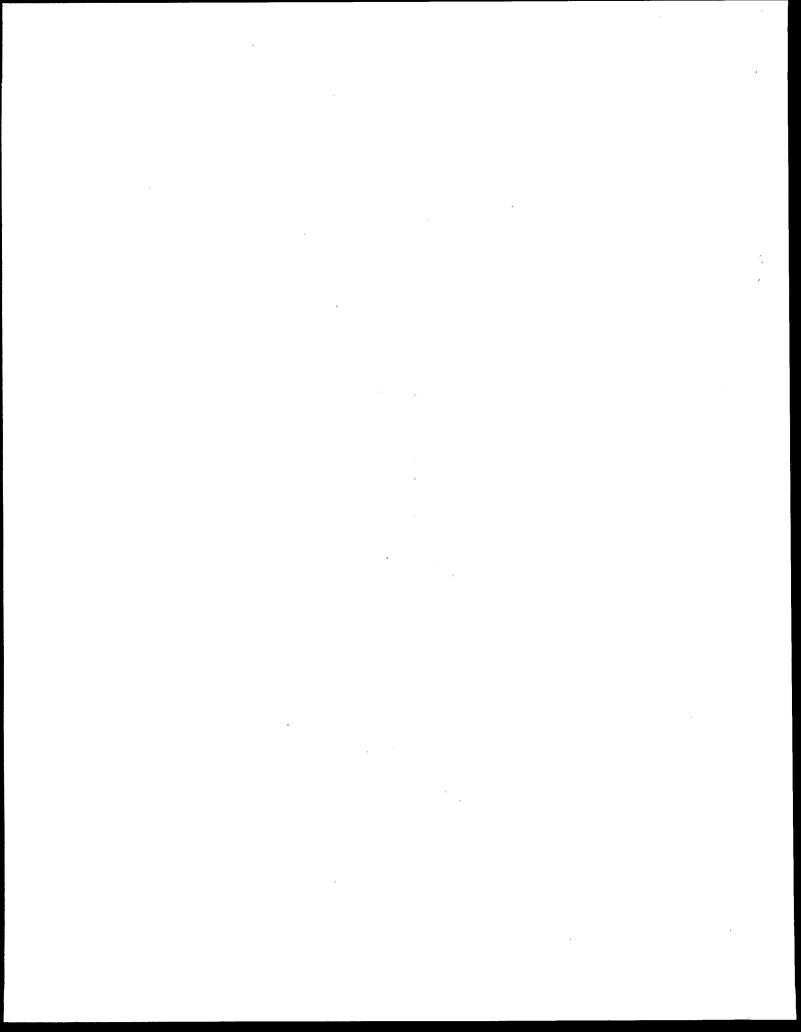
Vapor Treatment

- For captured volatiles
- Thermal
- Biological

Ground Water Control

Contamination containment

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